THEORETICAL ORGANIC CHEMISTRY

COHEN

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PREFACE

Some apology for the appearance of a new text-book of organic chemistry seems necessary; for in face of the multitude of its predecessors, the present volume can scarcely put forward the customary claim of supplying a "long-felt want."

Whilst the study of general principles should form the groundwork of every text-book, it is important, in a subject so essentially practical as organic chemistry, to maintain a careful balance between theory and practice. This has been my chief aim.

Organic chemistry has been so completely systematised—so few of the important links in the chain of facts are missing—that it offers great temptations to the teacher to place before the student a series of equations, qualified by the statement that the substances are *acted upon* by certain reagents, reduced with *nascent hydrogen*, *treated with* oxidising agents, etc., and other vague directions which leave to the student the task of evolving the practical details of the process for himself, and, what is worse, transforming organic chemistry into a series of barren formulæ and bald equations.

To avoid this as far as possible, a description of the common chemical reagents is introduced at the outset, and a number of simple experiments are described in detail concurrently with an account of many of the reactions.

The student is thus encouraged to study the reactions practically —a matter of very great consequence.

Another object of these experiments is to assist the teacher in his class demonstrations; for, with one exception (the preparation of zinc ethyl, which cannot be conveniently carried out in the classroom), they are devised so as to be completed during the lecture, or occasionally in a second lecture, but, in the majority of cases, to occupy not more than a few minutes. For a reaction done in a test-tube is just as effective didactically as a more sensational

experiment performed on a larger scale, and involving a greater expenditure of time.

The book, including all these experiments, represents my own course of about sixty lectures.

The production and uses of common materials, which come under our daily observation, are frequently relegated in some text-books of organic chemistry to a background of small print; in others they are entirely omitted. The reason for this is not clear, unless it arises from our present ignorance of the structural formulæ and relations of some of these compounds, and therefore from their lack of theoretical significance.

Whatever may be the cause, substances like lanoline, linseed oil, gelatine, the tannins, turpentine, etc., are usually treated in this stepmotherly fashion, and industrial processes, like tanning and sugar-refining, the manufacture of varnishes, petroleum, glycerine, soap, starch, etc., are dismissed with no more than an honourable mention.

I make no shadow of a claim to having accomplished the task of producing an ideal text-book. It is beset with many difficulties. One difficulty arises from the very completeness of the subject, for, to pursue the former metaphor, organic chemistry forms not only a chain, but an endless chain of facts. At the beginning, one is confronted with the difficulty that the simplest organic compound involves a knowledge of others of greater complexity. Certain assumptions have, in consequence, to be made, which upset at once the natural development of theories, and the gradual elaboration of the principles of structure, causing the text to bristle with cross references, which cannot be avoided. No attempt has been made to give anything like a complete set of methods for preparing even the more important of the substances described; on the contrary, the number has been carefully restricted to those which have a theoretical importance, or practical value. For example, the numerous methods which are generally introduced in describing the preparation of marsh-gas are greatly curtailed, and the complex reactions involving the use of zinc and magnesium alkyl compounds are grouped together in a later portion of the book, where the close analogy, which they exhibit, affords a better chance of their being understood and remembered.

Another difficulty in compiling a text-book proceeds from the introduction of theories, which cannot be exhaustively discussed within the limits of a small volume. I do not regard this as a real drawback; for a suggestion, which arouses curiosity, is better for the serious student, who will take a little trouble to read for himself, than an elaborate and complete discussion of the subject.

The idea of atomic space arrangement, which may now be regarded as one of the corner-stones of organic chemistry—almost equalling in importance the theory of quadrivalent carbon—is introduced at an early stage and kept constantly in view.

The modern theories which are included under the head of "physical chemistry" have at present only a subordinate interest in organic chemistry, and have therefore been very briefly mentioned with a reference to a text-book where the subject is methodically developed and, therefore, more easily followed.

The time seems to have come when certain well-worn names, which have done duty in the past, should now belong to history and vanish from the text-book. We no longer think of *esters* as compounds of ether with acids, as in the days of Berzelius, and I make no apology for having discarded the terms *ethereal salt* and *ether* applied in this sense.

The questions at the end of each chapter, many of which are drawn from University B.Sc. pass-papers, and from the papers of the Board of Education, South Kensington, are introduced in response to the exigencies of the present universal system of examination tests.

I wish to express my thanks to my friend and colleague, Professor Smithells, for much valuable advice, and to Mr. A. T. Simmons for his help in the correction of the proof sheets. I am also indebted to many friends and former students for details connected with technical processes with which they are engaged.

J. B. COHEN

THE YORKSHIRE COLLEGE
October, 1902

PREFACE TO THE SECOND EDITION

SINCE the first appearance of this book, ten years ago, new substances, processes, and reagents have been discovered, some of which find a place in the present edition, so that, so far as the elementary portions of the subject are concerned, the book has been brought up to date. A number of new experiments have also been added.

J. B. COHEN

THE UNIVERSITY, LEEDS
September, 1912

PREFACE TO THE THIRD EDITION

THE new developments in theoretical and applied organic chemistry which have taken place in the last few years have made it necessary to revise the former edition. Although there is little alteration in the general character of the book, considerable additions and modifications have been introduced.

J. B. COHEN

THE UNIVERSITY, LEEDS
September, 1928

PREFACE TO THE FOURTH EDITION

THE rapid growth of Organic Chemistry since the last revision by the late Prof. Cohen of this text-book, which has benefited so many students during the last forty years, has necessitated the preparation of an entirely revised edition. I have attempted to increase the usefulness of this work by adding new chapters on Stereochemistry and the Theory of Valency, while those on carbohydrates and proteins have been largely re-written and considerably expanded. The grouping together of heterocyclic and other complex substances into a new Part III has made it possible to separate the ureides from the aliphatic compounds, while the proteins are included in a new chapter on compounds of biological interest. Otherwise the general plan of the book has been preserved.

P. C. AUSTIN

THE TECHNICAL COLLEGE, PAISLEY
1942

CONTENTS

PART I. ALIPHATIC COMPOUNDS

PART III. COMPLEX COMPOUNDS

THEORETICAL ORGANIC CHEMISTRY

INTRODUCTION

The Growth of Organic Chemistry.—Organic chemistry is a branch of the science of comparatively recent development. Its real history begins about the year 1830. This statement does not imply that either organic substances or processes were unknown prior to that date. Numerous animal and vegetable products, sugar, starch, oils, gums, resins, etc., had been familiar commodities from the earliest times. Nations had long been acquainted with the methods of soap-making and of dyeing with vegetable dyes. A knowledge of fermentation and of distillation had produced alcohol, turpentine, essential oils, and acetic acid. Towards the close of the eighteenth century Scheele had added to the number of organic acids by the separation of malic acid from apples, citric acid from lemons, oxalic acid from sorrel, benzoic acid from gum benzoin, and lactic acid from sour milk, and he had further obtained glycerine from olive-oil. But, beyond the investigation of a certain number of natural products, organic chemistry had inspired as yet no sustained or systematic study. Indeed no progress could be made until the phlogistic theory had been abandoned, but with the dawn of the new century the true nature of combustion and of the composition of organic compounds were placed in their true light. It was Lavoisier who first showed that organic compounds consisted of carbon, hydrogen, and frequently oxygen, to which Berthollet afterwards added nitrogen. Even then the subject attracted little attention, mainly for the following reasons. Inorganic chemistry included mineral substances and their derivatives and inorganic compounds were distinguished by simplicity of composition. A substance consisting of two or three elements contained them in one, sometimes in two, rarely in three proportions. There was only one substance (common salt) consisting of

sodium and chlorine; only one substance (water) consisting of hydrogen and oxygen; only one compound (gypsum) containing calcium, sulphur, and oxygen; but, among organic compounds, substances so different in properties as alcohol, sugar, glycerine, acetic acid, oils, and fats, contained the same three elements, carbon, hydrogen, and oxygen, in different proportions. It was inconceivable that such differences in character and complexity could be evolved out of the same three elements without the intervention of some special power, and this was termed *vital force*. The living world, so it was held, laid aside the rules which governed inorganic chemistry. It possessed its own laws of combination and its own force of affinity. Its products were called *organic* to denote their origin from living or organised matter. The improved method of organic analysis introduced by Berzelius in 1814, by means of which he succeeded in making accurate determinations of the composition of some of the organic acids, revealed the simple atomic ratio of the constituent elements, and so removed one distinction between organic and inorganic compounds. But it was long before the complete synthesis of purely organic substances from inorganic materials shook the firmly-rooted belief in a vital force. It is true that Scheele, as far back as 1776, had obtained oxalic acid, hitherto only found in sorrel, from sugar and nitric acid; that Döbereiner, in 1822, had shown that tartaric acid on oxidation yields formic acid, which had been previously obtained by the distillation of ants with water; that in 1826 Hennel, an English apothecary, had synthesised alcohol, and that a little later (1828) Wöhler prepared urea, a purely animal product, from lead cyanate and ammonium chloride; but none of these artificial substances was entirely independent of an animal or vegetable origin. Even the cyanates were derived in the first instance from potassium ferrocyanide, in the preparation of which animal matter was employed. But, as year by year new synthetic products were added to the list of organic compounds, this last barrier which separated organic from inorganic chemistry was swept away, and organic chemistry became *the chemistry of carbon compounds*.

It was when organic chemistry had reached this stage in its history that it was stimulated into new life by the appearance in

1832 of the classical research of Liebig and Wöhler on "The Radical of Benzoic Acid," which, they truly said, "might shed a new light on the vast and unexplored region of organic Nature." [1]

Organic chemistry, which then comprised a few hundred substances derived from animal and vegetable sources, now includes some hundred thousand compounds, for the most part artificial products of the laboratory. Through what agency has this extraordinary development been accomplished? It may be traced to two causes. One is the discovery of the laws, first formulated by Kekulé in 1858, which underlie the structure of organic compounds. These laws have served not only to co-ordinate and link together in a simple fashion the great mass of organic substances; but have enabled chemists to predict with some certainty the existence of others yet unknown. The other cause is the industrial application of discoveries in organic chemistry (initiated by Perkin in 1856 by the introduction into commerce of the first coal-tar colour) wherein theory and practice have been happily blended to the great advantage of both. The art of the dyer has been entirely revolutionised by the introduction of artificial dye-stuffs, the skill of the surgeon has been marvellously aided by the discovery of anæsthetics and antiseptics. The photographer relies on organic "developers." Synthetic drugs of established purity are used in medicine, artificial essences in perfumery. Moreover, the organic chemist controls such industries as tanning and calico-printing, and the making of starch, soap, paper, paraffin, ink, glue and gelatine, rubber, explosives, etc.

The distinction between inorganic and organic chemistry, though now purely arbitrary, is still retained for reasons of convenience, but not because there exists any fundamental difference between the two branches of the science.

Reasons for the Distinction between Organic and Inorganic Chemistry.—The reasons for preserving this division are, in the first place, the large number and complexity of organic compounds. The number has already been referred to; the complexity of some of these compounds may be illustrated by the following examples :—

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[1] *Vide* Ladenburg's *History of Chemistry*, trans. by L. Dobbin. Clay, Edinburgh, 1905.

Turpentine,	$C_{10}H_{16}$
Cane-sugar,	$C_{12}H_{22}O_{11}$
Stearin,	$C_{57}H_{110}O_6$
Starch (soluble),	$(C_6H_{10}O_5)_x$

In the second place, organic chemistry has its peculiar reagents and processes, arising from the nature of the compounds and the variety of products to which they give rise. A solution of ferrous sulphate may be oxidised by weak or strong nitric acid, chlorine, bromine, potassium permanganate, hydrogen peroxide, etc., and one product, ferric sulphate, results; but the effect of these reagents on an organic substance like grape-sugar would probably be a different product in each case.

In the third place, the study of organic substances cannot be limited to a knowledge of their composition. Sulphuric acid is represented by the formula H_2SO_4, and that formula stands for one substance only; but the formula C_2H_6O stands both for ethyl alcohol and dimethyl ether. Such substances, which have different properties, but possess the same simple formula, are said to be *isomeric* (ἴσος, equal or like; μέρος, a part), and this is a striking characteristic of organic compounds. The formula $C_8H_{12}O_4$ represents 66 compounds.

It is obvious that, if we wish to distinguish between isomeric substances, we must learn something more than their mere composition. We must discover the different arrangement of the atoms in the molecule upon which the properties of the various isomeric compounds depend. We must determine, not only their composition, but their *structure* or *constitution*. In other words, we must find a *structural* or *constitutional* as well as a *simple* formula. This is one of the chief objects of organic chemistry. It may be accomplished by *disintegration*, or *cleavage*, *i.e.* breaking down the molecule into simpler parts; or by *synthesis*, *i.e.* building up the more complex substance from its simpler constituents. As a rule, disintegration precedes synthesis. When the former has revealed the structure of a compound, its synthetic production has been only a question of time. In this way many substances are now prepared artificially which were formerly known only as natural products. This has been the case with oil of bitter almonds, alizarin, indigo, Tyrian purple, grape-sugar, caffeine, camphor,

menthol, and a host of others. It may come to pass that albumin, the universal constituent of living matter, will one day be obtained synthetically; but it must be remembered that between the synthesis of the most complex of individual organic substances and that of the simplest living cell there exists, and probably always will exist, an impassable gulf.

CHAPTER I

PURIFICATION OF SOLIDS AND LIQUIDS

BEFORE it is possible to determine the constitution of an organic substance, it is first necessary to be assured that it consists of one individual, or in other words, that it is a pure substance. It is then analysed qualitatively and quantitatively, the weight of its molecule is determined, and finally its chemical behaviour is studied.

Crystallisation.—If the substance under investigation is a solid or mixture of solids, it may be purified by *crystallisation*. The majority of organic substances can be obtained in the crystalline form by employing a suitable solvent, or mixture of solvents. A suitable solvent is one which dissolves much more of the substance when hot than cold, so that the hot saturated solution deposits a quantity of the solid on cooling. The usual solvents are water, boiling-point (b.p.) 100°; methyl alcohol, b.p. 66°; ethyl alcohol, b.p. 78°; ether, b.p. 35°; acetone, b.p. 56°; chloroform, b.p. 61°; benzene, b.p. 80°; petroleum spirit, b.p. 70°–90°; ethyl acetate, b.p. 77°; acetic acid, b.p. 119°, etc.

It is sometimes convenient to use two miscible solvents, one of which dissolves the substance readily, and the other only slightly.

EXPT. 1.—Dissolve about 2 grams of acetanilide in 10 c.c. of absolute alcohol. No separation takes place on cooling. Add to the hot alcoholic solution 20 c.c. of hot water. On cooling crystals of acetanilide separate and fill the liquid.

If more than one substance is present, one of the substances may be soluble and the others insoluble in the solvent. Separation is then partially effected by *filtration*. If they all dissolve, as more frequently happens, it is unlikely that they will be equally soluble, and consequently the first crystals which separate from the hot saturated liquid will represent the least soluble portion. If the mother-liquors are now concentrated by evaporation, a second

crop of crystals will be deposited, which will contain a larger proportion of the more soluble constituent. The mother-liquors from these will contain a still greater proportion of the more soluble constituent and so on. By a repetition of this process, which is termed *fractional crystallisation,* the mixture may be separated more or less completely into its constituents. *Microscopic examination* will often show if the crystals are homogeneous or not by the difference in crystalline form. The process of crystallising requires practice and skill, and is one of the most important operations in organic chemistry.

Sublimation.—Another method of purification which is occasionally employed, is *sublimation.* The process may be carried out in various ways. One method is to place the substance in a large watch-glass on a sand-tray which is heated by a small flame. The substance is covered with a sheet of asbestos-paper, held in position by a second inverted watch-glass or funnel. The volatile substance sublimes on the asbestos-paper whilst the non-volatile compound remains on the watch-glass.

Distillation in steam may be used occasionally for effecting the separation of solids and liquids. An experimental illustration of the process will be given later (p. 417).

Melting-Point Determination.—It is well known that the presence of a "foreign ingredient" lowers the melting-point of a substance. Fusible metals are made on this principle. If we made various mixtures of two substances A and B and plotted their melting-points as ordinates and the quantities as abscissæ we should obtain a curve something like that in the accompanying Fig. 1. The melting-point of each would fall with successive additions of the second substance until it reached a minimum and would then rise until the second pure substance alone was present.

Successive crystallisations would show by a change or otherwise in melting-point if the substance were pure. Slow liquefaction is an indication that the substance is impure for the following reason: on cooling a mixture of two substances, the one that predominates would separate until the mixture of minimum melting-point (eutectic point) is attained, when the whole would solidify. On heating a mixed solid the reverse occurs, and if the process takes place slowly some of the more fusible mixture will melt, leaving

the purer and therefore higher melting substance. Thus the melting is protracted and may take place through a wide range of

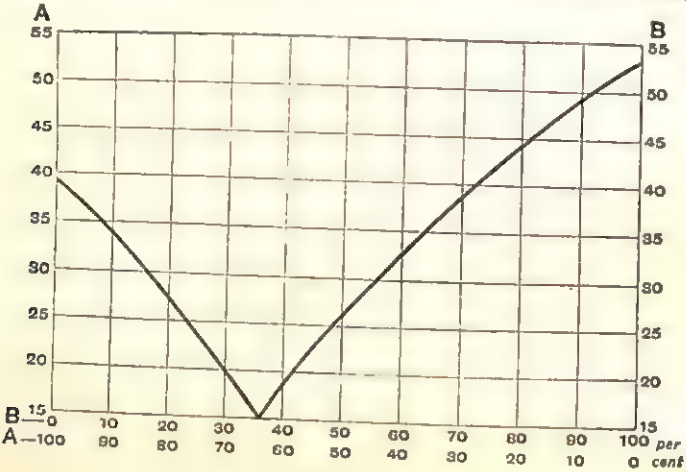


FIG. 1.

temperature. The identity of two substances having the same melting-point can be ascertained by fusing them together and then taking the melting-point which should remain unchanged.

The apparatus used for determining the *melting-point* is shown in Fig. 2. A small quantity of finely powdered substance which has been carefully dried is introduced into a capillary tube sealed at one end. The tube is attached to a thermometer so that the substance is level with the bulb. The attachment may be made by a narrow rubber ring, or by simply moistening the side of the capillary tube by contact with the thermometer bulb which has been dipped into the liquid. When pressed against the thermometer stem the capillary tube adheres.

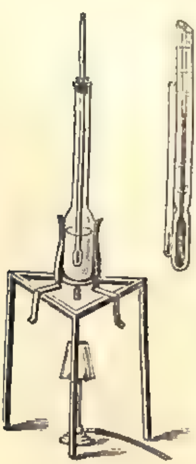


FIG. 2.

The thermometer passes through a cork inserted into a pear-shaped vessel with a long neck containing concentrated sulphuric acid or castor-oil. The vessel fits into a metal stand which can be placed upon a tripod, and is

heated very gradually by a small flame. When a certain temperature is reached, the substance, if pure, melts suddenly within a range of 1 or 2 degrees. When approaching the melting-point, it is desirable to remove the flame, or turn it very low, so that the rise of temperature is very gradual. As stated above, if the liquefaction is protracted it is an indication that the substance is not pure.

Some substances do not melt, but, on reaching a certain temperature, decompose. The purity of such substances can only be

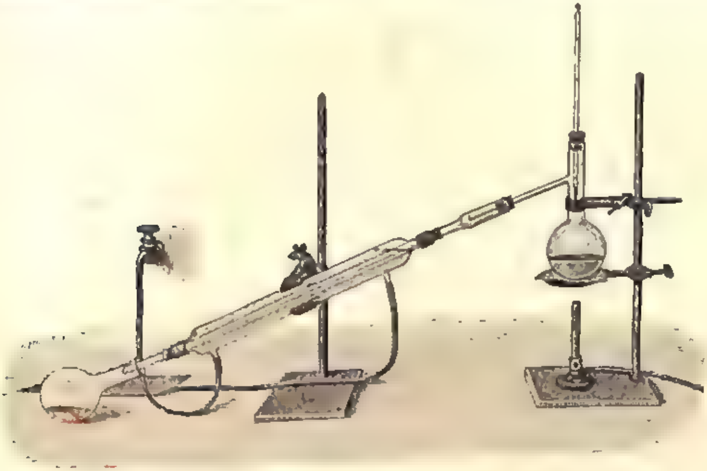


FIG. 3.—Apparatus for determining the boiling-point.

approximately gauged by repeated crystallisation and careful microscopic examination. It is difficult to establish with certainty whether substances like resins, dextrins, and proteins, which do not crystallise, are single individuals or not, and purification is rendered very troublesome.

Boiling-Point Determination.—Pure volatile liquids have a constant and definite *boiling-point*. This is ascertained by distilling the liquid in the apparatus shown in Fig. 3. It consists of a flask with a side-tube (distilling-flask), which is attached to a condenser. A second flask (receiver) is placed below the end of the condenser. A thermometer is inserted into the neck of the distilling flask.

A standard thermometer must be used, and correction made for barometric pressure, which is approximately 0·043° for every 1 mm. below 760 mm. (Landolt). A further correction is required for the thread of mercury which may project above the vessel. For this correction the following formula may be used:

$$N(T - t) \cdot 000154,$$

where T = apparent temperature in degrees Centigrade.

t = temperature of a second thermometer, the bulb of which is placed at half the length N above the vessel.

N = length of the mercury column in degrees from above the vessel to T.

0·000154 = apparent expansion of mercury in glass.

This correction may be avoided by using short (Anschütz) thermometers, in which the mercury thread is entirely immersed in the vapour.

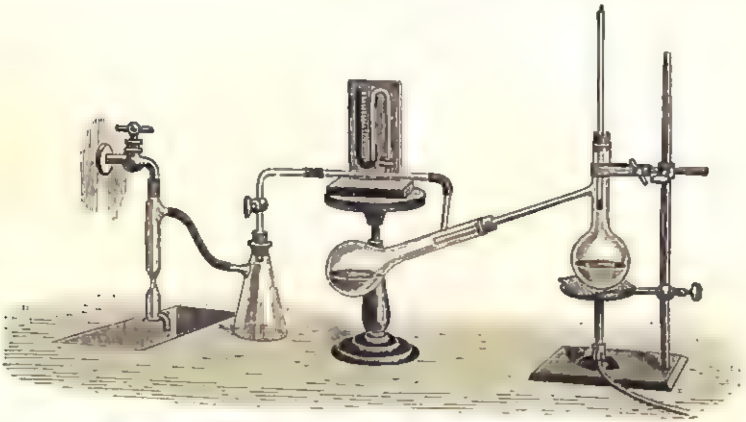


FIG. 4.—Distillation under diminished pressure.

A rough correction for points above 100° may be made by determining the boiling-points of pure organic substances, such as naphthalene, 216·6°, etc.

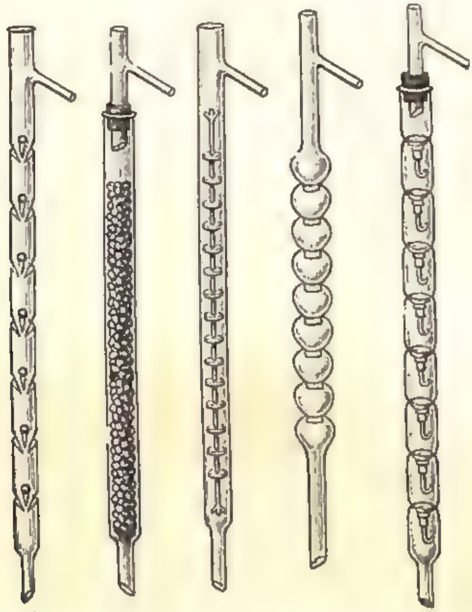
The liquid is then boiled, and the temperature noted as the liquid distils. If the liquid is pure, the temperature, indicated by the thermometer, during the distillation does not fluctuate. Some liquids of high boiling-point, like glycerol (glycerine), which, under atmospheric pressure, undergo decomposition near the boiling-point, may be distilled under diminished pressure, which naturally lowers the boiling-point. The simplest apparatus for effecting this operation is shown in Fig. 4. It consists of a distilling appar-

atus like that described, but in place of an ordinary flask a second distilling-flask serves for the receiver, the neck of which is tightly attached to the condenser, and the side-tube to a gauge and water-jet aspirator. Sometimes it is desirable to omit the condenser, and the side-tube of the distilling-flask is then inserted into the neck of the receiver.

Fractional Distillation.—If the liquid is not a single substance, but a mixture, it is often possible to separate the constituents by a single distillation, provided the boiling-points lie widely apart. The more volatile liquid first passes over, the temperature quickly rises, and the liquid of higher boiling-point distils. It is otherwise when a liquid consists of substances boiling at temperatures not very far removed from one another, especially in the case of chemically related substances, such as constitute petroleum and coal-tar naphtha. One distillation suffices only to produce a very incomplete separation, a portion of the less volatile liquid being carried over in the first distillate, together with the more volatile body, the temperature gradually rising throughout the distillation. In order to effect separation of the several substances, recourse is had to the method of *fractional distillation*. The liquid is distilled in a round flask, which is surmounted with a *fractionating column*, holding the thermometer. Various forms of fractionating columns are used (Fig. 5).

The effect of the column may be explained as follows. The vapour given off from a mixture of liquids contains, as a rule, a larger proportion of the more volatile constituent than the liquid. If this vapour is partly condensed in its ascent, the vapour above this condensed liquid will be still richer in the more volatile constituent. If, by a series of constrictions or diaphragms, the condensed liquid is obstructed in its return flow, a momentary equilibrium between liquid and vapour is established at each diaphragm, and the longer the column the greater will be the amount of the more volatile constituent in the last portion of vapour to undergo condensation. This passes off by the condenser, and is collected in the receiver. By this means a partial separation is effected, and the portions distilling within a range of a small number of degrees are collected in separate flasks. Each of these portions or fractions is redistilled, and collected within

still narrower limits of temperature, until at length the mixture is separated into certain portions, the boiling-points of which are nearly constant, and these may be regarded as pure.



A B C D E

FIG. 5 represents a series of simple and efficient fractionating columns or still-heads. A is that of Vigreux, in which the constrictions are formed by indenting the tube itself; B is Hempel's column and consists of a long wide tube filled with glass beads; C, D, and E are columns devised by Young and Thomas, the last being useful when large quantities of liquid have to be distilled. C contains a series of glass discs fused on to a rod, which can be removed from the tube; D has a series of pear-shaped bulbs blown on the stem, and E is a wide tube with a series of constrictions in each of which a small bent glass dripping tube is suspended in a gauze cup.

The following tables, I. and II., illustrate two series of fractional distillations of coal-tar naphtha containing a small quantity of paraffin boiling below 80°; benzene, b.p. 80°; toluene, b.p. 110°; and xylene, b.p. 140°. In the first fractionation (Table I.) the distillate is collected between every 5 degrees.

TABLE I.

A 71·5°–85°	B 85°–90°	C 90°–95°	D 95°–100°	E 100°–105°	F 105°–110°	G 110°–115°	Residue.
19 c.c.	53 c.c.	26 c.c.	15 c.c.	13 c.c.	17 c.c.	21 c.c.	33 c.c.

In the second fractionation (Table II.) each of the first distillates is redistilled and collected within a narrower range of temperature. Thus, the first fraction (A) is distilled until the thermometer registers 79°. Fraction B is then added, and the distillate divided into two fractions, 79°–81° and 81°–85°. Fraction C is added, and so forth. The new fractions, C′ and E′, are again fractionated. Ultimately, two fractions are obtained; B′ consisting of nearly pure benzene, and F′ of nearly pure toluene.

TABLE II.

	A′ below 79°	B′ 79°–81°	C′ 81°–85°	D′ 85°–105°	E′ 105°–108°	F′ 108°–110°	Residue.
A . . .	5 c.c.						
Added B .	—	42 c.c.	(10 c.c.*)				
,, C .	—	—	(9 c.c.*)				
,, D, E	—	—	—	50 c.c.	(11 c.c.*)		
,, F .	—	—	—	—	—	22 c.c.	42 c.c.
,, G .	—	—	—	—			
*Refractionated C′ .	—	12 c.c.	7 c.c.				
*Refractionated E′ .	—	—	—	—	6 c.c.	5 c.c.	
	5 c.c.	54 c.c.	7 c.c.	50 c.c.	6 c.c.	27 c.c.	42 c.c.

EXPT. 2.—Distil a mixture of 20 c.c. of alcohol, b.p. 78°, and 50 c.c. of water, b.p. 100°. The mixture will not inflame. Collect the first 10 c.c. of the distillate. The liquid now contains such a large proportion of alcohol that it readily takes fire.

If the fractional distillation has to be conducted *in vacuo* it is undesirable to interrupt the boiling in order to remove the receivers containing different fractions. Various forms of apparatus have

been devised for continuous fractional distillation under reduced pressure, one of which is shown in Fig. 6.

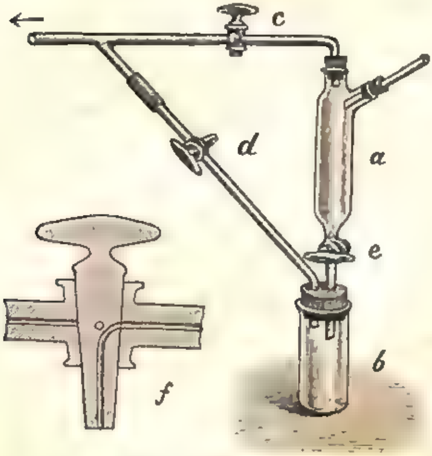


FIG. 6.—Receiver for fractional distillation under reduced pressure.

The apparatus (Fig. 6) consists of a double receiver, *a* and *b*; *c* and *e* are ordinary two-way taps, whilst *d* is a three-way tap pierced length-wise and crosswise as shown in section at *f*. The aspirator is attached to the limb marked with an arrow. During the distillation the taps *c* and *d* connect the apparatus with the aspirator, whilst *e* is closed. The distillate collects in *a*. When this fraction is to be removed, *c* is closed and *e* is opened. The liquid is thereby transferred to the second receiver *b*; *e* is now closed, *c* is opened, and *d* turned so as to let air into *b*; *b* may now be removed and replaced by a similar vessel, and the process continued. Fig. 7 needs little explanation. There are two or more receivers on one stem. By rotating the stem the distillate falls into one or other receiver. It should be borne in mind that the method of fractional distillation can only be applied to those mixtures whose boiling-point curves lie on a gradually ascending slope, as shown in (1), Fig. 8, where the quantities of the two substances are plotted against the boiling-points. But other curves are conceivable and are actually known where a given

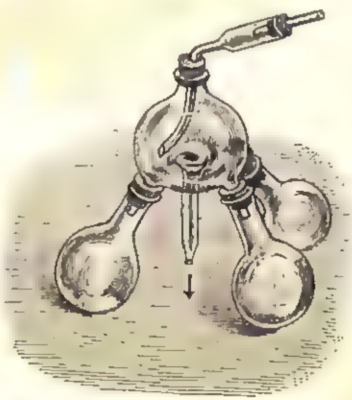


FIG. 7.—Receiver for fractional distillation under reduced pressure.

mixture shows a minimum (2) or maximum (3) boiling-point. In both these cases mixtures of definite composition and constant

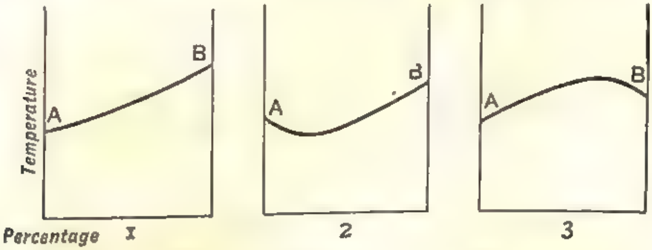


FIG. 8.

boiling-point, called **azeotropic mixtures,** are produced, and since they distil unchanged in composition separation of the two components is not possible. In case 2 **either** A **or** B (but not both) will remain, according to the composition of the original mixture, and the azeotropic mixture can be separated from the *distillate* by fractionation. In case 3 either A or B will distil first, the final residue being the azeotropic mixture of maximum boiling-point.

If, in a mixture of two liquids, one is soluble in water and the other not, like benzene and alcohol, the insoluble constituent may be separated by adding water and pouring the mixture into a *separating* or *tap-funnel* (Fig. 9). The benzene will separate and float above the water in which the alcohol remains dissolved. The aqueous layer is then drawn off and separated from the benzene.

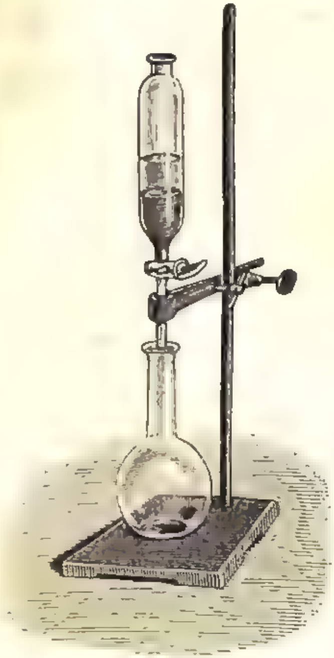


FIG. 9.—Tap-funnel for separating non-miscible liquids.

Extraction with ether etc.—Many organic compounds can be purified by taking advantage of the fact that they are much more soluble in an organic solvent than in water. In this way it is possible to avoid subjecting them to the prolonged heating which evaporation of water would necessitate. Ether, benzene and chloroform can all be used for extractions, since their solubilities in water are very low. Ether is most frequently used because it is easily removed at a rather low temperature and on account of its inert character. The aqueous mixture in which the compound has been prepared is shaken with small quantities of the ether in a separating funnel, when the compound will become distributed between the two liquid layers according to the well-known distribution law, which depends on the relative solubilities in the solvents. The two layers are then separated. Two or three extractions with small quantities of ether are more effective than one with the same total amount of ether. An ethereal extract floats upon, and a chloroform solution sinks below the aqueous layer. Since the extracts are wet, they must be dried by adding solid calcium chloride or anhydrous sodium sulphate to clear them. They are then filtered and the solvent is distilled off.

Questions on Chapter I

1. Give reasons for retaining organic chemistry as a separate branch of chemistry.

2. What is meant by *fractional crystallisation* and *fractional distillation?* With what object are these two processes employed?

3. Explain the principle of the fractionating column. Can the process of fractional distillation be employed in the separation of all mixtures of volatile liquids of different boiling-points?

4. How is the purity of organic liquids and solids ascertained?

5. Devise methods for separating the constituents in the following mixtures: (1) alcohol from water; (2) benzene from alcohol; (3) glycerol (glycerine) from water.

CHAPTER II

ANALYSIS OF ORGANIC COMPOUNDS

Qualitative Tests

Having prepared the substance in a pure state, the next step is to determine its constituent elements.

Carbon and Hydrogen.—Compounds of carbon are frequently inflammable, and when heated on platinum foil take fire or char. A safer test for carbon is to heat the substance with some easily reducible metallic oxide, the oxygen of which forms carbon dioxide with the carbon present, which is detected by passing the gas through lime-water. Hydrogen, if present, is at the same time converted into water, which condenses in drops on the cold part of the apparatus.

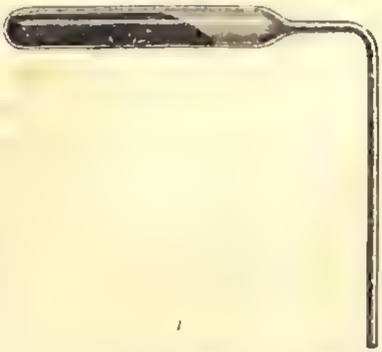


Fig. 10.—Apparatus for detecting carbon.

Expt. 3.—Take a piece of soft glass tube about 13 cm. long, and fuse it together at one end. Heat a gram or two of fine copper oxide, in a porcelain crucible for a few minutes to drive off the moisture and let it cool in a desiccator. Mix it with about one-tenth of its bulk of powdered sugar in a mortar. Pour the mixture into the tube, and draw out the open end, bending it at the same time into the form shown in Fig. 10. Suspend it by a copper wire to the ring of a retort stand, and let the open end dip into lime or baryta water. Heat the mixture gently with a small flame. The gas which bubbles through the lime-water turns it milky. Moisture will also appear on the sides of the tube, which, provided that the copper oxide has been thoroughly dried beforehand, indicates the presence of hydrogen in the compound.

Gases or volatile substances like ether and alcohol cannot of

course be examined in this way; but the gases or liquids may be burnt in a closed vessel, or the vapour led over a layer of red-hot copper oxide and then through lime-water.

The elements nitrogen, sulphur and the halogens are often combined with carbon in such a way that their presence can only be detected by subjecting the substance to drastic treatment in order to produce soluble ions of cyanide, sulphide or halide. The usual method is to heat them with metallic sodium, but it should be noted that it is dangerous to heat chloroform, carbon tetrachloride or polynitro-compounds with sodium. H. Middleton has described a method, which will be described later, whereby the use of sodium in analysis can be avoided altogether.

Nitrogen.—When nitrogenous organic compounds are heated with metallic sodium, sodium cyanide is formed, and the subsequent test is the same as for a cyanide (p. 215).

EXPT. 4.—Pour about 10 c.c. of distilled water into a small beaker. Place a little benzamide or *p*-toluidine in a small test-tube along with a piece of metallic potassium or sodium the size of a coffee bean, and heat them, at first gently, until the reaction subsides, and then strongly, until the glass is red-hot. Place the hot end of the tube in the small beaker of water. The glass crumbles away, and any residual alkali metal reacts with the water with a bright flash; all the cyanide goes into solution, whilst a small quantity of carbon remains suspended in the liquid. Filter through a small filter into a test-tube. Pour into the clear solution about 1 c.c. of ferrous sulphate solution, to which a drop of ferric chloride has been added, boil for a minute, cool, and acidify with dilute hydrochloric acid. A precipitate of Prussian blue indicates the presence of nitrogen.

In many cases nitrogen may be detected by heating the substance with soda-lime, when the nitrogen is evolved as ammonia.

EXPT. 5.—Grind up a small amount of acetamide with about four times its bulk of soda-lime; introduce the mixture into a test-tube, and cover it with a shallow layer of soda-lime. Heat the test-tube strongly, and at the same time hold a piece of moistened red litmus at the mouth of the tube. If it is turned blue, nitrogen is present.

Halogens.—Many halogen compounds impart a green fringe to the outer mantle of the non-luminous flame. A more delicate test is to heat the substance with copper oxide, which gives a vivid green coloration.

EXPT. 6.—Heat one end of a piece of thick copper wire in a bunsen flame, until it ceases to colour the flame green. Let it cool down a little, and then dip it into some halogen compound. Now heat again. A bright green flame, accompanied by a blue zone immediately round the oxide, indicates the presence of a halogen.

The halogen in the majority of organic compounds is not directly precipitated by silver nitrate. This may be seen by adding silver nitrate solution to chloroform. Only those compounds which, like the hydracids and their metallic salts, dissociate in solution into free ions give this reaction. If, however, the organic compound is first destroyed, and the halogen converted into a soluble metallic salt, the test may be applied. The substance is heated with pure lime, or with a fragment of metallic sodium or potassium, as in the test for nitrogen (Expt. 4, p. 18). The filtered solution is acidified with nitric acid, and silver nitrate added. A curdy white or yellow precipitate (provided no cyanide is present) indicates a halogen.

If nitrogen and chlorine are both present, both silver cyanide and silver chloride will be formed, and as they are very similar in properties, it is not easy to distinguish between them. One method is to add to the alkaline solution just enough *dilute* nitric acid to make the liquid slightly acid and then to boil off the liberated hydrogen cyanide. The addition of silver nitrate will then indicate a chloride. Another method is to add silver nitrate to the solution, previously acidified with dilute nitric acid without heating, and then to add a 5% solution of mercurous nitrate *drop by drop*. If a cyanide is present, the precipitate will first blacken; on addition of excess of mercurous nitrate solution the black compound will dissolve leaving white silver halide.

Sulphur.—The presence of sulphur in organic compounds may be detected by heating the substance with metallic sodium or potassium. The alkaline sulphide, when dissolved in water, gives a violet coloration with a solution of sodium nitroprusside.

EXPT. 7.—Heat a fragment of thiourea with a small piece of sodium in a test-tube until the bottom of the tube is red-hot, and place it in a small beaker of water, as described in the test for nitrogen (Expt. 4, p. 18). Filter the liquid and add a few drops of sodium nitro-prusside solution (p. 219).

Phosphorus and Arsenic.—These elements are comparatively rare constituents of organic substances. They may be detected by fusion with an oxidising mixture of sodium carbonate and potassium nitrate, which converts the phosphorus and arsenic into phosphate and arsenate of the alkali. The fused mass is dissolved in water, and the usual qualitative tests are applied.

Metals.—The substance is ignited to destroy all organic matter and the residual oxide or carbonate can then be analysed in the usual manner.

Oxygen.—There is no direct method for detecting the presence of oxygen in organic compounds.

Middleton's reactions.—For the detection of nitrogen use a mixture of 1 part of pure anhydrous sodium carbonate with 2 parts of the purest zinc dust instead of sodium. Mix a small sample of the substance with about 5 times its bulk of this reagent and heat it as with sodium. Proceed as before. If the zinc mixture be used for the detection of sulphur, the latter will not be found in the aqueous extract but will remain undissolved as zinc sulphide. The residue should then be acidified and the vapour tested with lead acetate paper. For halogens and sulphur the best reagent to use is a mixture of 9 parts of pure sodium carbonate with 1 part of pure sugar finely powdered. If the two reagents are mixed beforehand in bulk and stored in dry bottles they will last a very long time. The method has been well tested and found satisfactory.

Quantitative Analysis

The qualitative examination of an organic compound is followed by a quantitative analysis.

Carbon and Hydrogen.—The principle of the method for the quantitative estimation of carbon and hydrogen is that described under the qualitative test (p. 17), but the substance and the products of combustion, viz. carbon dioxide and water, are weighed.

The water is absorbed by calcium chloride or by pumice impregnated with concentrated sulphuric acid and the carbon dioxide by a concentrated solution of caustic potash. Caustic soda is not used in this case on account of the rather low solubility of sodium bicarbonate which if precipitated would choke the slender inner tubes of the absorption bulbs.

The original form of the apparatus was devised by Liebig (1831). A hard glass tube is filled two-thirds full of coarse copper oxide, a small boat containing a weighed quantity of the substance is then introduced, and behind it a roll of oxidised copper gauze, as shown in Fig. 11.

The tube is placed in a combustion furnace and the end nearest

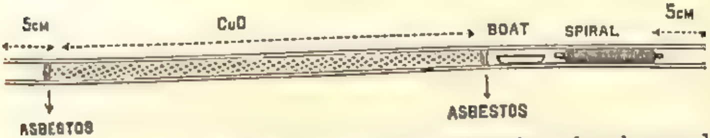


FIG. 11.—Arrangement of tube for the estimation of carbon and hydrogen.

to the boat is connected with two gas-holders, one containing oxygen and the other air. The gases are purified by passing them through U-tubes containing soda-lime and concentrated sulphuric acid. The other end of the tube is attached to a weighed U-tube containing calcium chloride (Fig. 12), and an apparatus, two forms of which are shown in Figs. 13 and 14, containing a strong solution

FIG. 12.—Calcium chloride tube.

of caustic potash, which is also weighed. The arrangement of the whole apparatus is shown in Fig. 15.

The layer of copper oxide is made red-hot, and then the roll of copper gauze, whilst a slow current of oxygen from the gas-holder is passed through the tube. The substance is then gradually heated and burnt.[1] The water, which is formed, collects in the

[1] The full details of the process are described in the Author's *Practical Organic Chemistry* (Macmillan).

calcium chloride tube and the carbon dioxide in the potash apparatus.

When the substance is entirely burnt, the oxygen is cut off and

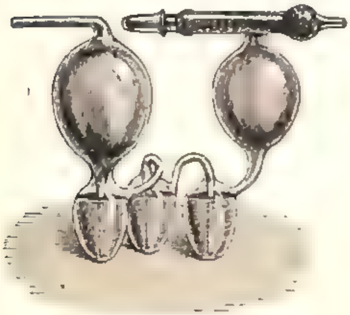


FIG. 13.—Potash apparatus.

FIG. 14.—Potash apparatus.

a current of air passed through the apparatus. The calcium chloride tube and potash apparatus are then detached and weighed.

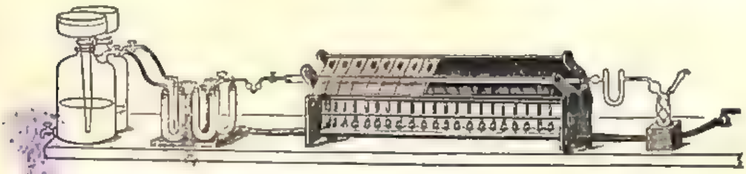


FIG. 15.—Combustion apparatus for estimating carbon and hydrogen.

The results are calculated in percentages of carbon and hydrogen as follows :—

w is the weight of substance taken.
a is the increase in weight of the potash apparatus.
b is the increase in weight of the calcium chloride tube.

$$\frac{12 \times a \times 100}{44 \times w} = \text{per cent. of carbon.}$$

$$\frac{2 \times b \times 100}{18 \times w} = \text{per cent. of hydrogen.}$$

Example I.—0·1830 gram of substance gave 0·6118 gram of CO_2 and 0·1315 gram of H_2O.

$$\frac{12 \times \cdot 6118 \times 100}{44 \times \cdot 1830} = 92{\cdot}3 \text{ per cent. of carbon.}$$

$$\frac{2 \times \cdot 1315 \times 100}{18 \times \cdot 1830} = 7{\cdot}9 \text{ per cent. of hydrogen.}$$

As the two quantities added together make, within the limits of experimental error, 100 per cent., no oxygen is present.

Example II.—0·1510 gram of substance gave 0·1055 gram of CO_2 and 0·068 gram of H_2O.

$$\frac{12 \times \cdot 1055 \times 100}{44 \times \cdot 1510} = 19{\cdot}05 \text{ per cent. of carbon.}$$

$$\frac{2 \times \cdot 068 \times 100}{18 \times \cdot 1510} = 5{\cdot}00 \text{ per cent. of hydrogen.}$$

Here the difference between 100 and the aggregate precentages of carbon and hydrogen is 75·95, and must be due to the presence of oxygen, seeing that no other elements were found.

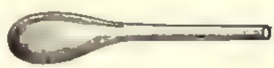


FIG. 16.

Volatile liquids are inclosed in small bulbs (Fig. 16), which are carefully weighed. The liquid is then introduced, and the neck sealed. Before placing the bulb in the tube, the neck is scratched with a file and opened. If the organic substance contains nitrogen, the latter may be liberated in the form of one or other of its oxides. These would be absorbed in the potash apparatus, and cause an error in the amount of carbon. A roll of copper gauze is therefore brought into the front end of the combustion tube, which, when red-hot, reduces the oxides of nitrogen. The free nitrogen then passes through unabsorbed. When halogens or sulphur are present in the organic compound, they are also liable to be absorbed either in the free state, or in combination with oxygen in the potash apparatus. In this case, fused lead chromate broken up into small pieces must be used in place of the copper oxide in the combustion tube. The halogens and sulphur are retained by the lead, the former as halide salt, and the latter as lead sulphate.

Nitrogen.—Nitrogen is usually estimated by one of the following methods: by burning the substance with copper oxide in an atmosphere of carbon dioxide, and collecting the free nitrogen over potash solution (Dumas); by heating the substance with soda-lime, and estimating the ammonia evolved (Will and Varrentrapp); or by decomposing the substance with concentrated sulphuric acid at a high temperature, and converting the nitrogen into ammonium sulphate (Kjeldahl). Whilst Dumas' method is universally applicable, the other two processes cannot always be employed, and only give trustworthy results when the nitrogen in the compound is directly combined with carbon and hydrogen.

DUMAS' METHOD.—A combustion tube closed at one end is filled as shown in Fig. 17. A layer of magnesite is first introduced, then some coarse copper oxide. This is followed by the substance

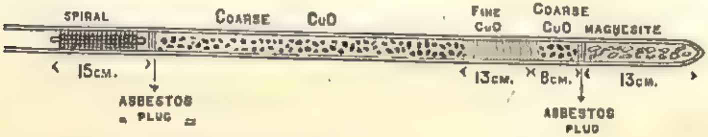


FIG. 17.—Open combustion tube for estimating nitrogen.

well mixed with fine copper oxide. The tube is then partly filled with coarse copper oxide, and finally a spiral of metallic copper is introduced. The copper spiral serves to reduce any oxides of nitrogen, which would be otherwise absorbed by the potash solution. The open end of the tube is attached to a Schiff's *nitrometer* (Fig. 18). It consists of a graduated tube, surmounted with a tap and furnished with two side tubes, one being attached to the combustion tube, and the other to a reservoir containing potash solution. By opening the tap and raising or lowering the reservoir, the solution may be introduced into the graduated tube or removed into the reservoir. The reservoir is first lowered, and the potash solution run out of the tube. The magnesite is then heated until the air is driven out of the combustion tube. The nitrometer is then filled with potash, and the combustion is carried on in the manner described in the estimation of carbon and hydrogen. Nitrogen collects in the nitrometer, and when the evolution of gas

slackens, the magnesite is again strongly heated to drive out the last trace of nitrogen gas. Instead of using a closed tube with magnesite for evolving carbon dioxide, it is convenient to use an open combustion tube, and to attach it, either to a second tube containing sodium bicarbonate (Fig. 19), which is heated in a second small furnace or to a Kipp or other apparatus for evolving carbon dioxide.

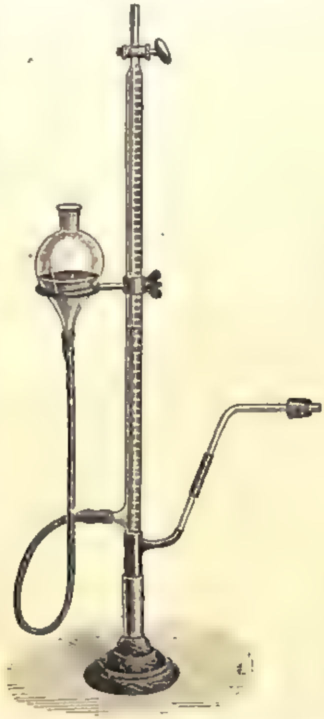


FIG. 18.—Schiff's nitrometer.

When the combustion is complete, the liquid in the reservoir of the nitrometer is brought on a level with that in the graduated tube and the volume measured. The height of the barometer and the temperature are also noted.

The percentage of nitrogen is calculated as follows :—

v is the observed volume of nitrogen.
B is the height of the barometer in mms.
t is the temperature.
f is the vapour tension of the potash solution, which may be taken without serious error to be equal to that of water.

The volume, corrected to 0° and 760 mms., will be given by the following expression :—

$$\frac{v \times 273 \times (B - f)}{(273 + t)\,760}.$$

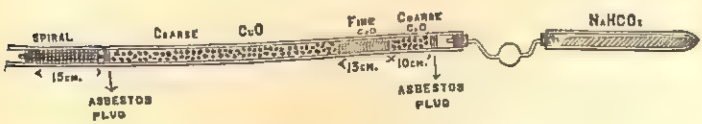


FIG. 19.—Arrangement of tube for nitrogen estimations.

As the weight of 1 c.c. of nitrogen at 0° and 760 mms. is 0·00126 gram, the percentage weight of nitrogen in the substance w will be given by the expression—

$$\frac{v \times 273 \times (B - f)}{(273 + t)\,760} \times \frac{\cdot 00126 \times 100.}{w}$$

Example.—0·206 gram of substance gave 18·8 c.c. of moist N at 17° and 756 mms. (f at 17° = 14·5 mms.).

$$\frac{18{\cdot}8 \times 273 \times (756 - 14{\cdot}5) \times \cdot 126}{(273 + 17) \times 760 \times \cdot 206} = 10{\cdot}56 \text{ per cent. of N.}$$

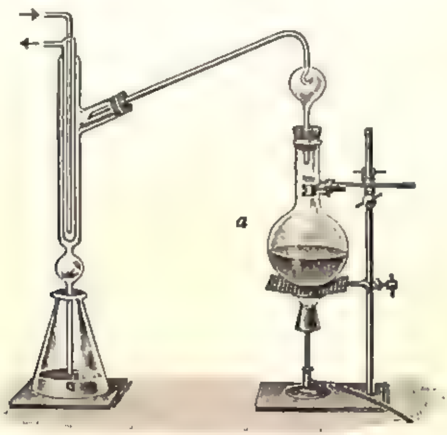


FIG. 20.—Apparatus for estimating nitrogen by Kjeldahl's method.

KJELDAHL'S METHOD.—The substance is boiled for a time with concentrated sulphuric acid and potassium sulphate, a little potassium permanganate or persulphate being subsequently added. The acid, which at first darkens in colour, then becomes colourless. The nitrogen is now present as ammonium sulphate. The liquid is then made alkaline with caustic soda and boiled to drive off the ammonia, the ammonia being absorbed in a receiver containing a known volume of standard hydrochloric or sulphuric acid. The apparatus is shown in Fig. 20. The flask *a* contains the ammonium sulphate, caustic soda is introduced, the liquid is boiled, and the water and ammonia are condensed and collected in the flask *b* containing the acid.

The quantity of ammonia is determined by titrating the acid with standard alkali. The strength of the original acid being known, the difference will give the amount of ammonia.

WILL AND VARRENTRAPP'S METHOD.—This method, which has been to some extent replaced by Kjeldahl's process, depends upon the fact, already mentioned, that nitrogenous substances yield

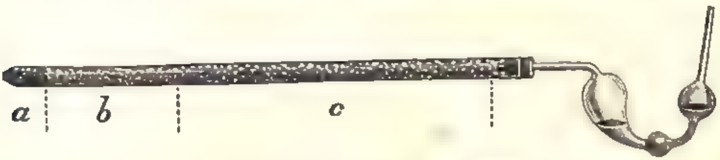


FIG. 21.—Apparatus for estimating nitrogen by Will and Varrentrapp's method.

ammonia when heated with soda-lime. The operation is conducted as follows :—A combustion tube closed at one end is filled with a short layer of soda-lime mixed with zinc dust, *a*, then with the weighed substance mixed with soda-lime, *b*. The remainder of the tube is filled up with soda-lime, *c*, and attached to absorption bulbs containing a known volume of standard acid. The tube is placed in a combustion furnace. The long layer of soda-lime is first heated to redness, then the substance, and finally the zinc dust, which, in contact with soda-lime, evolves hydrogen, and sweeps out any residual ammonia. The arrangement of the apparatus is shown in Fig. 21.

FIG. 22.—Sealed tube used in Carius' method.

The Halogens.—CARIUS' METHOD.—The method of Carius, which is usually employed, consists in oxidising the substance with fuming nitric acid under pressure in presence of silver nitrate. The silver halide which is formed is then separated by filtration and weighed. A thick-walled tube is sealed at one end, and a few c.c. of fuming nitric acid introduced together with the silver nitrate crystals. The substance is weighed in a narrow tube and slipped in. The tube is then sealed before the

blow-pipe in such a way that a thick capillary is formed, which enables it to be subsequently opened (Fig. 22). It is then placed in a hot-air furnace, as shown in Fig. 23, and is heated for several hours at 200° or above, according to the nature of the compound. The furnace is then allowed to cool, the pressure released by holding the capillary end in the flame until the glass softens and is perforated by the pressure within. The tube can then be safely

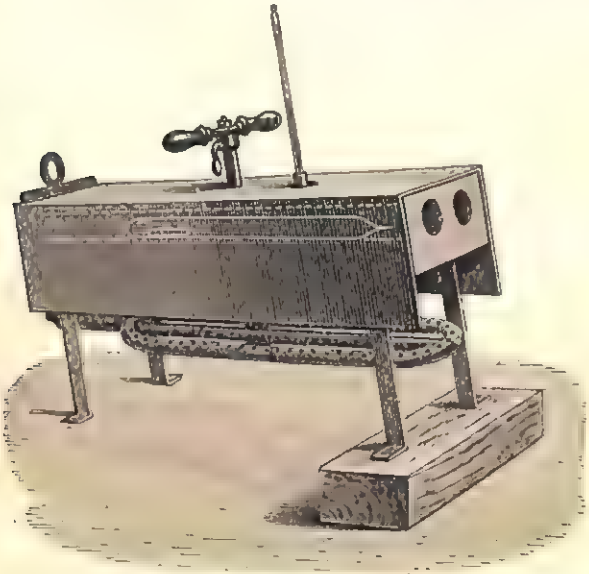


FIG. 23.—Hot-air furnace with a Carius' tube.

opened. The contents are washed out, and the silver halide filtered, dried, and weighed.

PIRIA AND SCHIFF'S METHOD.—There are some substances which are incompletely decomposed with fuming nitric acid under the conditions described above, and the results are consequently too low. In this case the substance is mixed with quicklime and sodium carbonate in a small platinum crucible which is inverted in a larger one, the space between the two being filled in with the mixture of sodium carbonate and lime. The crucibles are heated over the blow-pipe, the contents allowed to cool, and dissolved in

excess of dilute nitric acid. The halogen is then precipitated with silver nitrate and estimated in the usual way.

Example.—0·151 gram of substance gave 0·134 gram AgBr.

$$\frac{0·134 \times 80 \times 100}{188 \times 0·151} = 37·51 \text{ per cent. of bromine.}$$

Sulphur.—CARIUS' METHOD.—The process is essentially the same as that just described.

The compound is oxidised in a sealed tube with fuming nitric acid, but without the addition of silver nitrate. The resulting sulphuric acid is then precipitated and weighed as barium sulphate.

Example.—0·2518 gram gave 0·2638 gram $BaSO_4$.

$$\frac{0·2638 \times 32 \times 100}{233 \times 0·2518} = 14·39 \text{ per cent. of sulphur.}$$

QUESTIONS ON CHAPTER II

1. How would you show that alcohol contains carbon, hydrogen, and oxygen?

2. Calculate the percentage composition of cane-sugar, $C_{12}H_{22}O_{11}$.

3. Describe and explain the difference in the method employed in the estimation of chlorine in chloroform and calcium chloride.

4. Calculate the weight of carbon dioxide and water, and the volume of nitrogen under normal conditions, obtainable from 0·2 gram of urea, CH_4N_2O.

5. Describe a method for the estimation of nitrogen in organic compounds.

6. Calculate the percentage of nitrogen estimated by Kjeldahl's method from the following data: 0·5 gram of the substance was decomposed and distilled with caustic soda, and the ammonia collected in 50 c.c. of normal sulphuric acid. The acid then required 33·6 c.c. of normal caustic soda solution for neutralisation.

7. Calculate the percentage of carbon, hydrogen, and oxygen from the following data: 0·2046 gram of substance gave, on combustion, 0·2985 gram of carbon dioxide and 0·1255 gram of water.

8. By what methods can a carbon compound be shown to contain (*a*) nitrogen, (*b*) chlorine, (*c*) phosphorus?

9. Describe any method commonly used for the determination of sulphur in an organic compound.

10. In the estimation of nitrogen by the soda-lime method, 0·2102 gram of benzamide was taken and the evolved ammonia absorbed in 25 c.c. of half-normal sulphuric acid solution; the residual acid required 21·52 c.c. of half-normal soda (NaOH) solution for neutralisation. What was the percentage amount of nitrogen in the benzamide?

CHAPTER III

EMPIRICAL AND MOLECULAR FORMULÆ

Empirical Formula.—From the results of an analysis it is possible to calculate the relative number of atoms of the different elements present in an organic compound. This is done by dividing the percentage weights by the atomic weights of the elements. If we take the first example of an analysis of carbon and hydrogen (p. 22), and divide the numbers representing the per cent. of carbon and hydrogen by the respective atomic weights of these elements, we obtain approximately the same quotient—

$$C\ \frac{92 \cdot 3}{12} = 7 \cdot 7.$$

$$H\ \frac{7 \cdot 9}{1} = 7 \cdot 9.$$

The ratio of the number of carbon to hydrogen atoms is 1 : 1, and the substance may be represented by the formula CH. This is known as the *empirical formula*. The real formula of the substance is without doubt some multiple of the empirical formula; but an analysis can give no further information upon this point. Let us now take the numbers in the second example, and divide by the atomic weights. We obtain the following quotients—

$$C\ \frac{19 \cdot 05}{12} = 1 \cdot 59.$$

$$H\ \frac{5}{1} = 5.$$

$$O\ \frac{75 \cdot 95}{16} = 4 \cdot 74.$$

To find the smallest whole numbers standing in the same ratio

as these quotients, we may divide by the smallest quotient of the series—

$$C\ \frac{1{\cdot}59}{1{\cdot}59} = 1.$$

$$H\ \frac{5}{1{\cdot}59} = 3{\cdot}14.$$

$$O\ \frac{4{\cdot}74}{1{\cdot}59} = 2{\cdot}98.$$

The empirical formula is, therefore, approximately CH_3O_3. By way of confirmation, the percentage composition of the substance is calculated from this formula and compared with the analytical results. If the difference in the numbers falls within experimental errors (0·2 to 0·3 per cent.), the formula is accepted as correct.

	Found.	Calculated for CH_3O_3.
C	19·05 . . .	19·04
H	5·00 . . .	4·76
O (by diff.) .	75·95 . . .	76·20
	100·00	100·00

The analytical numbers satisfy in this case the calculated percentages.

The results for hydrogen are often rather high on account of incomplete drying of the air or oxygen and those for carbon may be low if the gas bubbles too rapidly through the absorption tubes. The difficulty of displacing *all* the air by carbon dioxide makes the nitrogen results rather high.

Micro-Analysis.—When substances are only available in minute amounts they can be subjected to micro-analysis, which is similar in principle and rapidly carried out, but it requires special apparatus including a micro-balance and very careful manipulation.

Molecular Formula.—To find the molecular formula of an organic compound we must determine the *molecular weight* of the substance, or the weight of the molecule compared with that of the atom of hydrogen as the unit. The methods may be divided into physical and chemical.

Physical Methods

There are several methods, all of which depend upon certain hypotheses.

Vapour Density Method.—According to Avogadro's hypothesis, equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. Suppose that an equal volume of hydrogen and of the substance, X, of unknown molecular weight in the form of gas, be weighed under the same conditions. If the volume of hydrogen contain 5 molecules, the volume of X will contain 5 molecules, or, in other words, the ratio of the weight of these two volumes will be the ratio of the weight of the molecule of hydrogen and of the molecule of X.

Volume of Hydrogen.

Volume of X.

But the ratio of the weights of equal volumes of the gas X and hydrogen is the density of the gas. It is represented by the expression—

$$\Delta = \frac{W_x}{W_h},$$

in which W_x and W_h are the weights of equal volumes of substance and hydrogen, respectively. Now, as the molecule of hydrogen consists of two atoms, the density, which is the molecular weight of the substance compared with *one molecule* of hydrogen, must be multiplied by 2 to make it represent the ratio in respect of *one atom* of hydrogen.

$$\text{M.W.} = \Delta \times 2 = \frac{W_x}{W_h} \times 2.$$

Seeing that the weight of any volume of hydrogen under varying conditions of temperature and pressure is known (1 c.c. = 0·00009 gram at 0° and 760 mm.), it is only necessary to ascertain the weight of a given volume of the vapour or gas, from which the weight of the same volume of hydrogen may be calculated. There

are four methods for determining vapour densities. In the case of permanent gases, the gas is weighed in a large globe according to the method of Regnault. Victor Meyer's method and Hofmann's method consist in ascertaining the volume occupied by a given weight of the vaporised substance. According to Dumas' method, the weight of substance occupying a given volume is determined.

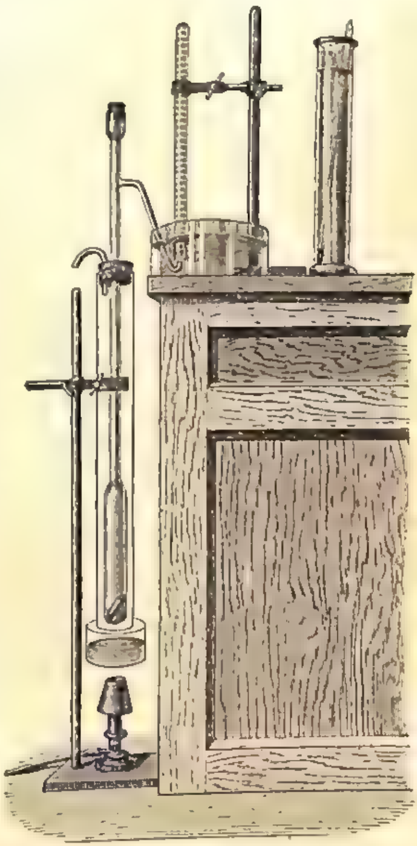


FIG. 24.—The Victor-Meyer vapour density apparatus.

REGNAULT'S METHOD.—The method is only used for permanent gases, and has a very limited application in organic chemistry. It consists in counterpoising a large globe, first evacuated, and then filled with the gas and finally with hydrogen, against a similar globe having the same capacity, the difference being adjusted by weights. The second globe is employed to neutralise the effects due to varying temperature, pressure, and moisture, which would greatly alter the buoyancy of the single globe, whereas when two globes are employed, the changes affect them in the same way, and do not interfere with the actual weight of the gases.

AIR DISPLACEMENT, OR VICTOR MEYER'S METHOD.—This method is universally employed; for, whilst yielding fairly accurate results, it is quickly performed and demands only small quantities of material. It consists in rapidly vaporising a known weight of the substance at a constant temperature at least 40°–50° above its

boiling-point in a special form of apparatus, which admits of the displaced air being collected and measured. The volume occupied by a given weight of the substance under known conditions is thus ascertained, and from these data the density is calculated. The apparatus is shown in Fig. 24. It consists of an elongated glass bulb with a narrow stem and a capillary side-tube. It is provided with a well-fitting rubber cork. The apparatus is clamped within an outer jacket of tin-plate or copper (represented as transparent in the figure) which holds the boiling liquid required to produce a constant temperature.

The substance, if liquid, is introduced into a small stoppered glass bottle known as a Hofmann bottle (Fig. 25). The dry bottle with the stopper is carefully weighed and then filled with liquid. The stopper is inserted, and the bottle re-weighed. It should hold about 0·1 gram of substance. The side-tube of the apparatus dips under water contained in a glass dish. The liquid in the jacket is boiled, and when the temperature is constant, *i.e.* when no bubbles pass out of the side-tube, a graduated tube filled with water is inverted over the end of the side-tube and clamped. The small bottle containing the substance is then dropped into the apparatus, and the cork tightly inserted. A stream of air bubbles passes into the graduated tube, and when they cease, the tube is carefully transferred to a cylinder of water, and after a time the volume, the temperature of the water, and the barometric pressure are observed.

FIG. 25.—Hofmann bottle.

EXPT. 8.—Thoroughly dry the apparatus by blowing air through it, and introduce a small quantity of clean dry sand previously heated, to break the fall of the Hofmann bottle. The bulb of the outer jacket is filled two-thirds full of water. The burner below should be protected from draughts by a chimney. To avoid inconvenience arising from the steam, a split cork, into which a bent glass tube is inserted, is pushed loosely into the open end of the jacket. Whilst the water is boiling steadily, the substance is weighed. Chloroform, b.p. 61°, or pure and dry ether, b.p. 34°·5, may be used for the experiment. Try if the temperature is constant, and fix the graduated tube in position. Remove the stopper of the Hofmann bottle before dropping it in. Transfer the tube to a cylinder, and read off the volume, after adjusting the level of the water within and without.

The density is calculated as follows :—

If v is the volume, t the temperature, B the barometric pressure, and f the vapour tension of water at $t°$, then the corrected volume is given by the formula—

$$\frac{v \times (B - f) \times 273}{760 \times (273 + t)}.$$

This multiplied by 0·00009, the weight of 1 c.c. of hydrogen, gives the weight of hydrogen occupying the same volume as the vaporised substance, from which the density, $\Delta = \frac{W_x}{W_h}$, is obtained.

Example.—0·1146 gram gave 36·3 c.c. at 11° and 752 mm. $f = 10$ mm. at 11°.

$$\frac{36{\cdot}3 \times (752 - 10) \times 273 \times 0{\cdot}00009}{760 \times 284} = 0{\cdot}00306.$$

$$\frac{0{\cdot}1146}{0{\cdot}00306} = 37{\cdot}4.$$

$$\text{Molecular weight} = 37{\cdot}4 \times 2 = 74{\cdot}8.$$

If substances of higher boiling-point have to be vaporised, the water in the outer jacket is replaced by other liquids of correspondingly higher boiling-point, such as xylene, b.p. 140°, aniline, b.p. 182°, ethyl benzoate, b.p. 211°, amyl benzoate, b.p. 260°, diphenylamine, b.p. 310°, etc.

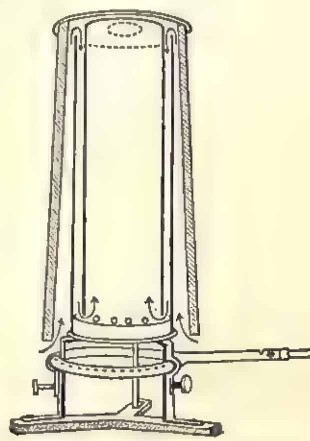


FIG. 26.—Lothar Meyer air-bath.

A Lothar Meyer air-bath (Fig. 26) is, however, much more convenient for obtaining constant high temperatures. It consists of three concentric metal cylinders, the outer one being coated with non-conducting material. They are so arranged that the heated air from a movable ring burner passes between the two outer cylinders (shown in section in the figure), and descends to the bottom of the central cylinder, into which it has access through a ring

of circular holes. The hot air is thoroughly mixed by this zig-zag flow and the temperature is equalised. The bulb of the displacement apparatus is clamped in the interior cylinder, and a thermometer is fixed beside it.

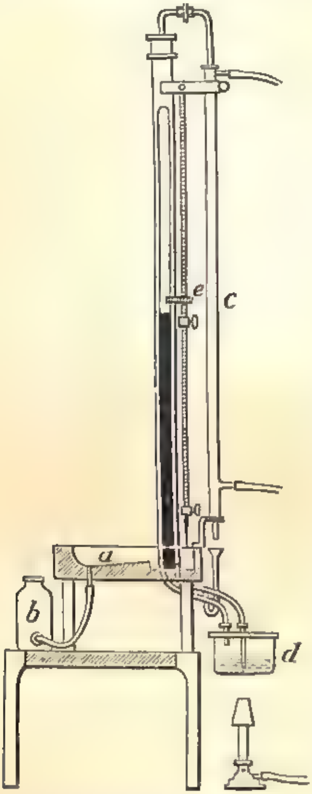


FIG. 27.—Thorpe's Hofmann apparatus.

HOFMANN'S METHOD.—This method is very accurate, and requires only small quantities of material; but it is troublesome to manipulate. It consists in vaporising at a constant temperature a known weight of substance above the mercury column of a barometer. The vapour is under reduced pressure, and substances may therefore be vaporised below their ordinary boiling-points. It admits also of substances being vaporised, which decompose under ordinary pressure. A long tube marked in millimetres, and calibrated so that the volume corresponding to the mm. divisions is known, is filled with mercury and inserted in a mercury trough. The height of the mercury is noted and the weighed substance contained in a Hofmann bottle is introduced. The tube is heated by an outer jacket, through which the vapour of a liquid of constant boiling-point circulates. The rise of temperature drives the stopper out of the small bottle and vaporises the contents, and this causes the mercury to descend to a certain point where it remains stationary. The point is read off on the scale, and from this the volume and pressure is ascertained. The temperature is also noted. The apparatus shown in section in Fig. 27 represents *Thorpe's modification* of Hofmann's apparatus.

It has a small mercury trough, *a*, from which the greater part of the mercury may be withdrawn into the movable reservoir, *b*,

during the operation, and remain there unwetted by the substance (the mercury requires to be dried after each operation). The tube is heated throughout its length, and the mercury in the tube is therefore at one temperature. The upright, *c*, is hollow, and serves the double purpose of a support and condenser, returning the condensed vapour to the boiling vessel, *d*. The barometer-tube is etched at one point only, which represents a measured volume. It is calibrated from this point, and the millimetres which correspond to a certain volume are measured on an adjustable metal scale, *e*.

Example.—0·0518 gram of substance occupied 52·5 c.c. at 100°; barometric height 752·5 mms.; height of mercury column 484 mms.; vapour tension of mercury at 100° 0·74 mm.; coefficient of expansion of mercury 0·00018. The volume is reduced to 0° and 760 mms. as follows:—The barometric pressure is the difference between the first and second readings of the mercury column. But the second reading represents the column at 100°. This is corrected by taking the difference and multiplying by (100 × 0·00018). From this the vapour tension of mercury at 100° = 0·74 must be deducted. The expression will then be—

$$W_h = \frac{52{\cdot}5 \times \{[752{\cdot}5 - 484\,(1 - 0{\cdot}018)] - 0{\cdot}74\} \times 273}{760 \times 373} \times 0{\cdot}00009.$$

$$\Delta = \frac{0{\cdot}0518}{0{\cdot}00125} = 41{\cdot}4.$$

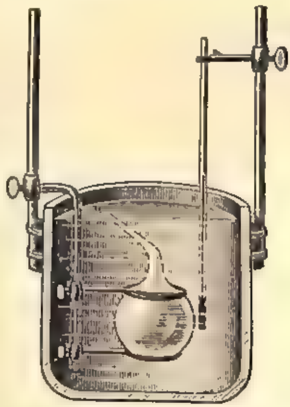


FIG. 28.—Dumas' vapour density apparatus.

'DUMAS' METHOD.—In point of accuracy and simplicity it offers no advantage over Victor Meyer's method, and requires a much larger amount of material. As a practical method, in connection with organic chemistry, it is obsolete. A glass bulb is used of about 200 c.c. capacity with a narrow neck (Fig. 28). The weight of the bulb having been found, a few c.c. of the liquid under investigation are introduced. The bulb is then heated in a bath (water or paraffin) to at least 40°–50° above the boiling-point of the substance. As soon as vapour ceases to issue, the narrow neck is drawn out and sealed. The temperature of the bath is noted. As the pressure is practically constant throughout the operation, it may be omitted in the calculation. The bulb is cooled and

weighed with the drawn-out end of the neck. The point is then broken off under water, which rushes in and fills the bulb, with the exception of a small bubble. The bulb is then filled up and weighed, and the capacity determined from the weight of water.

Example.—Weight of the bulb, temp. 15·5°	. .	23·449 grams.
,, ,, ,, and vapour at 100°		23·720 ,,
Capacity		178 c.c.

As the vapour has been weighed in air, the true weight will be the apparent weight of the vapour plus that of the displaced air, just as the true weight of mercury when weighed in water is the apparent weight plus the weight of the volume of displaced water. W_x will be—

$$23{\cdot}720 - 23{\cdot}449 + \frac{178 \times 273}{288} \times 0{\cdot}001293 = 0{\cdot}4892.$$

The weight of an equal volume of hydrogen at 100°, W_b, will be given by the expression—

$$\frac{178 \times 273 \times 0{\cdot}00009}{373} = 0{\cdot}01172.$$

$$= \frac{0{\cdot}4892}{0{\cdot}01172} = 41{\cdot}7.$$

There are many substances which cannot be volatilised without undergoing decomposition, and for which the above methods are not adapted. The molecular weights of such substances may be determined by the freezing- and boiling-point methods of Raoult.

The Cryoscopic or Freezing-point Method (Raoult).—The freezing-point (cryoscopic) method and boiling-point (ebullioscopic) method of Raoult depend upon the general principle that equimolecular solutions lower the vapour pressure to the same amount. Supposing we plot the change in vapour pressure with temperature for ice and water in the form of a curve, and then do the same after dissolving in it a small quantity of substance. The new curve will run nearly parallel with the first (Fig. 29).

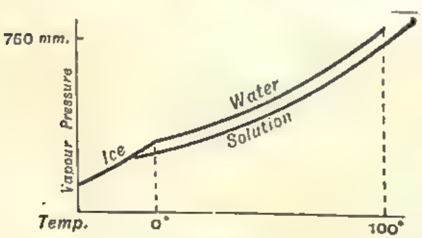


FIG. 29.

It will cut the vapour pressure curve for ice at some point below 0° and reach atmospheric pressure above 100°; in other words,

the addition of a soluble substance will lower the freezing-point and raise the boiling-point. Not only so, but if an equal molecular proportion of another substance were dissolved in the same quantity of water, precisely the same effect would be observed.

EXPT. 9.—The lowering of vapour pressure by equimolecular solutions may be demonstrated by inverting three barometer tubes over clean mercury and introducing into the torricellian vacuum by means of hooked pipettes about 0·5 c.c. each of the following three liquids:

(1) anhydrous ether; (2) a solution of 4 grams of phenol in 10 c.c. of anhydrous ether; (3) a solution of 10·8 grams of bromoform in 10 c.c. of anhydrous ether.

The second and third tubes, which contain equimolecular solutions, will show an equal depression, which is, however, less than that in the first containing the solvent.

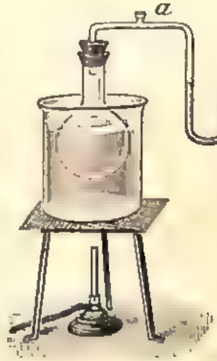


FIG. 30.

EXPT. 9*a*.—To show the elevation of boiling-point when a salt is dissolved in a pure solvent the apparatus (Fig. 30) may be used. It consists of a dry flask attached to a bent tube containing coloured water which serves as a gauge. The tube is furnished with an outlet *a* which can be closed with a plug. The flask is placed in an outer vessel of water. After the water has been boiling for two or three minutes, the outlet *a* is closed and when the gauge shows a steady pressure a quantity of common salt is added to the outer vessel. The cooling effect of the salt will cause at first a contraction, which will be very shortly followed by a permanent expansion, indicated by a rise in the open limb of the gauge.

The above rule of Raoult does not, however, apply to salts, acids, etc., which appear to dissociate in certain solvents, nor to substances which form molecular aggregates or *associate* in solution. Moreover the solutions must be so dilute that the observed depression or elevation of temperature amounts to only a fraction of one degree, although no such restriction need be applied to the calculations. Thus the depression observed for a solution containing 1 gram of urea in 100 gms. of water is only 0·31° C. If we multiply this by 60, the molecular weight of urea, the product (18·6° C.) is called the *molecular depression* for water and can be used for aqueous solutions of other compounds. The molecular

depression C can also be obtained by calculation from thermodynamical data [1] according to the expression :—

$$C = \frac{0{\cdot}02 T^2}{L}$$

in which T is the absolute temperature of the freezing-point and L the latent heat of fusion of 1 gram of the solvent in calories.

If w is the weight of substance and W the weight of solvent, d the depression of the freezing-point, and C the coefficient for the solvent determined for the standard conditions (*i.e.* for the weight of substance which produces 1° depression in 100 grams of solvent) the molecular weight, M, is given by the following expression :—

$$M = \frac{100\, Cw}{dW}.$$

The values of C for the common solvents in use are as follows :—

Water . .	18·8,	Benzene .	50,
Acetic Acid .	39,	Phenol .	75.

The form of apparatus, known as the *Beckmann apparatus*, is shown in the accompanying Fig. 31. It consists of a glass jar furnished with a stirrer. The cover of the jar has a wide slit to admit the stirrer, and a circular aperture with clips to hold a wide test-tube.

Within the wide test-tube is a narrower one, which is held in position by a cork. The narrow test-tube is sometimes furnished with a side-tube for introducing the substance. It is provided with a stirrer. A Beckmann thermometer completes the apparatus. This is fixed through a cork so that the bulb nearly touches the bottom of the tube, a wide slit being cut in the side of the cork for moving the stirrer. The Beckmann thermometer is of special construction, and requires explanation. As the method involves

[1] *Vide* van't Hoff, *Zeitschr. Phys. Chem.*, i. p. 481; Ostwald, *Outlines of General Chemistry*, chap. vi. p. 139 (Macmillan); J. Walker, *Introduction to Physical Chemistry*, chap. xviii. p. 176 (Macmillan).

merely an accurate determination of small differences of temperature, it is not requisite to know the exact position on the thermometer scale. The Beckmann thermometer registers 6 degrees, which are divided into hundredths. The little glass reservoir at the top (*a*, Fig. 31) serves the purpose of adjusting the mercury column to different parts of the thermometer scale by adding or removing mercury from the bulb. Eight to ten grams of solvent are introduced into the inner tube and weighed. The freezing-point of the solvent is then determined by cooling the outer vessel with water or ice below the freezing-point of the solvent. The solvent is slightly supercooled and then stirred. As soon as crystals begin to separate, the thermometer rises, and reaches a maximum which represents the freezing-point of the solvent. The operation is repeated for confirmation, and then a carefully weighed amount of the substance introduced. As soon as the substance has dissolved, the freezing-point is again determined as before, and this time a lower temperature will be indicated. A further quantity of substance may be added, and a new determination made.

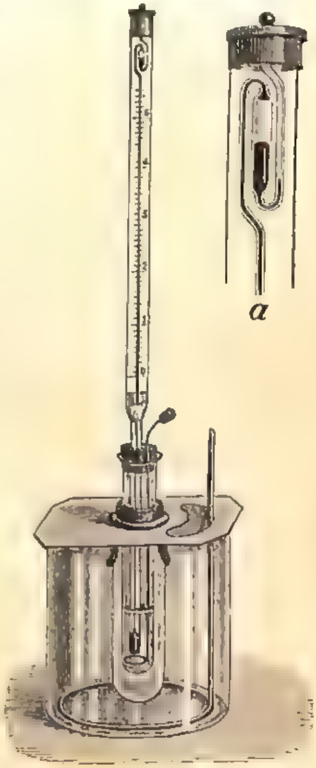


FIG. 31.—Beckmann's freezing-point apparatus.

Example.—Using the same solvent (benzene), and adding successively three quantities of substance (naphthalene), the following numbers were obtained :—

	w.	W.	*d.*	M.	Mean.
1	0·0985	9·7	0·403	126	125·3
2	0·0729	9·7	0·305	123·2	
3	0·1193	9·7	0·486	126·8	

M, the molecular weight in the fifth column, is calculated as follows:—

It is first necessary to find the weight of substance which, when dissolved in 100 grams of solvent, will lower the freezing-point 1°.

The weight of substance w in 100 grams of solvent is given by the expression—

$$\frac{0{\cdot}0985 \times 100}{9{\cdot}7}.$$

As the proportion between the substance and the solvent is unchanged, no effect is produced on the freezing-point.

The weight of substance in 100 grams of solvent required to lower the freezing-point 1° is

$$\frac{0{\cdot}0985 \times 100}{9{\cdot}7 \times 0{\cdot}403}.$$

Here it is assumed that the depression of the freezing-point is proportional to the weight of dissolved substance.

The above expression multiplied by 50, the coefficient for the solvent (benzene), gives the molecular weight

$$M = \frac{0{\cdot}0985 \times 100 \times 50}{9{\cdot}7 \times 0{\cdot}403}.$$

FIG. 32.—The Eijkman depressimeter.

THE EIJKMAN DEPRESSIMETER. — For rapid, but less accurate, determinations, the apparatus of Eijkman may be used, which is shown in Fig. 32. It consists of a small vessel, into the neck of which a thermometer is ground. The thermometer is of the Beckmann type, but divided into twentieths of degrees. Phenol, melting-point (m.p.) 42° is usually employed as the solvent. The vessel and thermometer are weighed. Phenol melted on the water-bath is poured in to within about 5 c.c. of the neck, the thermometer inserted, and the apparatus weighed again. The melting-point of the phenol is then ascertained by warming it until melted, and allowing it to cool in the cylinder, where it is occasionally shaken until crystallisation sets in. The weighed substance is now introduced, and the freezing-point determined as before.

The Boiling-point Method (Raoult.)—The boiling-point of a liquid is found to be affected like the freezing-point by the presence of a dissolved substance—that is, the boiling-point of a given quantity of a liquid is *raised* the same number of degrees by dissolving in it the same number of molecules of different substances, or, in other words, such weights of these substances as represent

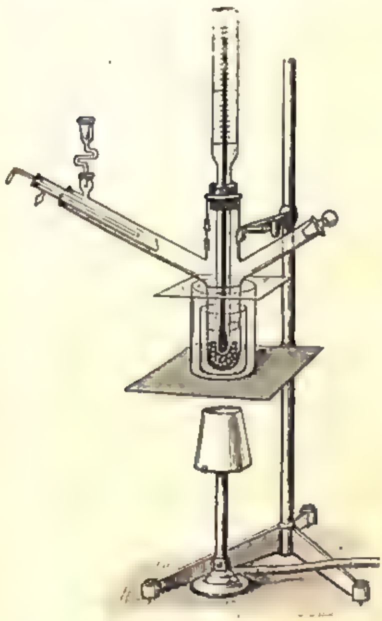


FIG. 33.

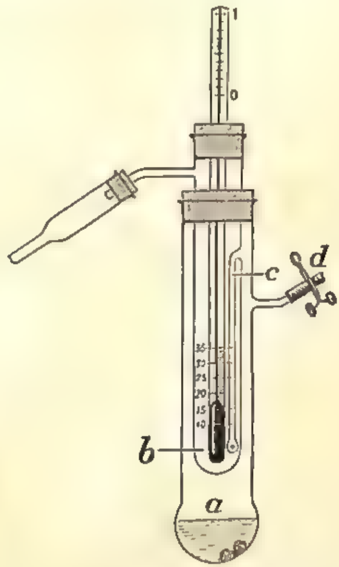


FIG. 34.—Landsberger-McCoy apparatus.

the ratio of their molecular weights. These facts were first clearly demonstrated by Raoult. One form of apparatus for determining molecular weights by this method is that of Beckmann, shown in Fig. 33. Another is that of Landsberger, shown in Fig. 34.

BECKMANN'S APPARATUS consists of a boiling tube furnished with two side pieces, one of which is stoppered and serves to introduce the substance, and the other acts as a condenser. The boiling-tube stands on an asbestos pad and is surrounded by two short concentric glass cylinders surmounted by a mica plate. A Beckmann thermometer is inserted through a cork in the neck

of the tube. The thermometer is similar in construction to that used for freezing-point determinations, but it has a smaller bulb. The boiling-point of the solvent is first ascertained. The burner is lighted and the temperature regulated so that the liquid boils briskly. The temperature being constant, it is noted, and a weighed pellet of the solid substance is dropped into the boiling tube through the side piece without interrupting the boiling. The boiling-point rises, and after a short time will remain stationary. The temperature is again noted. A second and third determination may be made by introducing fresh pellets of the substance.

As in the freezing-point method, the molecular weight is calculated from the weight of substance required to raise the boiling-point of 100 grams of solvent 1°, and the result is multiplied by a coefficient, depending upon the solvent. The following is a list of solvents commonly employed, and their coefficients :—

Water	5·2
Alcohol	11·5
Ether	21·1
Acetic Acid	25·3
Benzene	26·7
Aniline	32·2
Chloroform	36·6
Nitrobenzene	50·1

The molecular weight is determined from the formula

$$M = \frac{100Cw}{dW},$$

in which w is the weight of substance, W that of the solvent, d the rise of boiling-point, and C the coefficient. Although the method is able to dispose of a greater number of convenient solvents than are adapted for freezing-point determinations, it is never so accurate, mainly on account of the difficulty of avoiding fluctuations in the boiling-point, due to radiation, to the dripping of cold liquid from the condenser, and to barometric fluctuations.

LANDSBERGER'S APPARATUS.—The apparatus, modified by Walker and Lumsden, and by McCoy,[1] is shown in Fig. 34.

[1] *American Chem. Journ.* (1900), vol. 23, p. 353.

The pure solvent is contained in the outer jacket, *a*, and the solution in the inner vessel, *b*. On boiling the liquid in the outer jacket, the vapour passes by the tube *c*, fused to the inside of the inner vessel, into the solution. The temperature of the solution is raised to the boiling-point by the latent heat given out by condensation of some of this vapour when it reaches the inner vessel. The vapour from the inner vessel passes away to a condenser. The boiling-point of the solvent is first determined, and a weighed quantity of the substance is then introduced. After the boiling-point has become constant, the contents of the inner vessel are weighed, and the weight of the solvent estimated by deducting the weight of substance. If great accuracy is not desired and a number of consecutive readings are required, the inner vessel may be graduated in cubic centimetres, and the volume of solvent read off by interrupting the boiling for a moment before the introduction of each fresh portion of substance. When the boiling is interrupted, the pinch-cock, *d*, on the side-tube of the jacket, must be opened to prevent the liquid running back from the inner vessel, *b*, into the outer jacket.

Chemical Methods

Molecular Weight of Organic Acids.—The basicity of an organic acid being known, the molecular weight can be obtained from the equivalent weight, which is determined either by direct titration of a weighed amount of the acid against standard alkali or by analysing the silver salt. Since organic acids are usually very weakly ionised a solution of caustic alkali must be used for the titration and $n/10$ or $n/5$ baryta is most convenient, since it is free from carbonate and gives therefore a sharp end-point with phenolphthalein. The silver salts are easily prepared by adding a solution of silver nitrate to a solution of the ammonium salt, prepared by boiling a solution of the acid with excess of ammonia until the liquid is neutral. They are rather insoluble and are therefore easily precipitated and when washed and dried are pure and anhydrous, but they are darkened on exposure to light and are easily decomposed. When ignited in a crucible a residue of pure silver remains, from the weight of which the equivalent weight is calculated. The precipitate is carefully washed and dried. A portion is

then weighed and ignited, and the metallic residue of silver weighed.

If W is the weight of salt, w the weight of silver, and n the basicity of the acid, the molecular weight of the silver salt is determined from the following formula :—

$$\frac{W \times 108n}{w}.$$

The molecular weight of the acid is then obtained by deducting n atoms of silver and adding n atoms of hydrogen.

Example.—0·3652 gram silver salt of a monobasic acid gave 0·172 gram of silver.

$$\frac{108 \times 0{\cdot}3652}{0{\cdot}1720} = 229{\cdot}3.$$

This represents the molecular weight of the silver salt. As it contains one atom of silver in place of one atom of hydrogen (being a monobasic acid), 108, the atomic weight of silver must be deducted and 1 added for the atom of hydrogen.

$$M = 229{\cdot}3 - 108 + 1 = 122{\cdot}3.$$

Molecular Weight of Organic Bases.—The organic bases (B) form, like ammonia, crystalline chloroplatinates with platinic chloride, of the general formula, $B_2H_2,PtCl_6$. By estimating the amount of platinum present in the salt, it is possible to calculate the molecular weight of the platinum compound, and, consequently, that of the base. The base is dissolved in a slight excess of moderately strong hydrochloric acid, and platinic chloride added. The chloroplatinate is precipitated as a yellow, crystalline powder resembling the ammonium salt, and is carefully washed and dried. A portion is then weighed and ignited in a crucible and weighed again. The molecular weight of the salt is calculated from the weight w of the platinum and W of the salt, according to the formula (the atomic weight of platinum being 195)—

$$\frac{W \times 195}{w}.$$

To determine from this the weight of the base, it is necessary to deduct from the molecular weight of the salt that of H_2PtCl_6,

and as 2 molecules of the base are contained in the salt, the result is halved.

Example.—0·7010 gram of a mono-acid salt gave 0·2303 gram platinum.

$$\frac{0{\cdot}7010 \times 195}{0{\cdot}2303} = 594{\cdot}2.$$

This represents the molecular weight of the salt, from which the weight of H_2PtCl_6 must be deducted and the result halved.

$$M = \frac{594{\cdot}2 - 409{\cdot}9}{2} = 92{\cdot}15.$$

One or other of the above physical and chemical methods for determining molecular weights will be found applicable to the majority of organic compounds. Only such substances are excluded as, being neither acids nor bases, are non-volatile or insoluble in any solvent. It is obvious that examples of this kind are rare. The molecular weight can only be approximately estimated by breaking up the compound into simpler constituents of known molecular weight. Such is the case with the starch molecule, which is non-volatile, and decomposes on dissolving in water. The molecular weight of soluble starch (p. 311) has been attempted by the cryoscopic method. It appears that the insoluble starch molecule from which soluble starch is formed has not a smaller, but probably a larger, molecular weight. Cellulose, which cannot be dissolved unchanged in any solvent, is another example of a substance the molecular weight of which cannot be determined. Its formula is therefore written $(C_6H_{10}O_5)_n$.

Questions on Chapter III

1. A substance gave the following analytical result:—C = 54·5; H = 9·09; O = difference.

A vapour-density determination by V. Meyer's method gave the following result: 0·1 gram of the substance displaced 27 c.c. of air measured at 15° and 745 mm. pressure (vapour tension at 15° = 12·7 mm.). Determine the molecular formula.

2. The following two results were obtained with Landsberger's boiling-point apparatus, using alcohol as solvent. Calculate the mean molecular weight of the substance.

Weight of substance.	Volume of solvent.	Rise of b.p.
1·01 grm.	24·2 c.c.	0·535°
1·01 grm.	25·3 c.c.	0·519°

The sp. gr. of alcohol at the b.p. = 0·7422.

3. 0·341 gram of the silver salt of a tribasic acid left on heating 0·2151 gram of silver. Calculate the molecular weight of the acid.

4. Calculate the molecular weight of a mono-acid base from the following data: 0·3557 gram of the platinum salt gave 0·117 gram of platinum.

5. What is the empirical formula of a compound having the following percentage composition: C = 23·58, H = 3·28, Cl = 23·23, N = 18·40, S = 21·00, O = 10·51? What precautions must be taken in the estimation of carbon and hydrogen in the above substance?

6. Find the empirical formula of the substance of which the analysis is given in Question 7 on p. 29.

7. Calculate the molecular weight of grape-sugar determined by the cryoscopic method from the following data: 10 grams of substance dissolved in 73·12 grams of water lowered the freezing point 1°·45. C = 18·8.

8. Describe Hofmann's vapour density method. What are its advantages and disadvantages?

9. Describe three distinct methods of arriving at the molecular weight of acetic acid.

10. Given a non-volatile, neutral, solid organic compound, how would you proceed to determine its molecular weight?

11. Calculate the empirical formula of a compound having the composition: C = 85·71 per cent.; H = 14·29 per cent. Describe the methods you would employ for the determination of the number of carbon and hydrogen atoms in the molecule of the substance in the event of its being (*a*) a gas, (*b*) a liquid, or (*c*) a solid.

12. The percentage composition of a liquid, containing carbon, hydrogen, and oxygen, was deduced from the following numbers:—0·300 gram when submitted to combustion with copper oxide gave 0·574 gram of carbon dioxide and 0·351 gram of water. The vapour density was 23 compared with hydrogen as unity. What is the formula of the liquid?

13. A monacid organic base, containing only hydrogen, nitrogen, and carbon, gave the following numbers on analysis:—0·186 gram gave 0·528 gram of carbon dioxide and 0·126 gram of water; 0·596 gram of its platinichloride yielded on ignition 0·195 gram of platinum. Calculate the molecular formula of the substance (Pt = 195).

CHAPTER IV

CONSTITUTION AND CLASSIFICATION

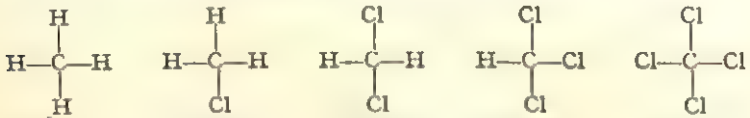
Constitution.—Having ascertained the molecular formula of a substance from its analysis and molecular weight, something may be learned about its structure in relation to other compounds of known constitution. By the constitution of a compound we mean the actual arrangement or distribution of the atoms in the molecule. It frequently happens that several different compounds have exactly the same molecular composition but differ from one another in properties. Such compounds are said to be **isomeric.** Thus dimethyl ether and ethyl alcohol both have the same molecular formula, C_2H_6O, but different constitutions. The atoms are differently linked in the two isomers. Sometimes compounds may have the same empirical formula but different molecular formulae. In that case the more complex molecules are called **polymers.** Thus benzene, C_6H_6, is a polymer of acetylene, C_2H_2; while acetic acid, $C_2H_4O_2$, lactic acid, $C_3H_6O_3$, and glucose, $C_6H_{12}O_6$, are all polymers of formaldehyde, CH_2O. Isomerism is of such frequent occurrence that we have to take it into consideration at a very early stage. Frequent references will be found to isomerism in the subsequent chapters. The mode of linking of an oxygen atom often provides a useful clue to structure, as many compounds consist solely of carbon, hydrogen, and oxygen. Now, if oxygen, which is bivalent, is combined with hydrogen to form the univalent radical hydroxyl, –OH, it cannot be linked to another hydrogen atom without forming water, thus leaving no room for anything else. Hydroxyl must then be linked either to oxygen or to carbon. Now, the group –O·OH is rather unstable and has oxidising properties. Usually we shall find, then, that –OH is combined with carbon, thus: ⋮C–OH. But oxygen may be combined with carbon in two other ways: either as :C:O or as ⋮C–O–C⋮. The particular type of union can be determined with the aid of the chlorides of

phosphorus. The hydroxyl group is replaced by one chlorine atom, the doubly linked oxygen atom by two chlorine atoms, and the third type of compound will not react at all. By these simple reactions the problem of constitution becomes simplified. Other groupings require individual treatment, which will be described from time to time.

The Linking of Carbon Atoms.—Since carbon is quadrivalent, its atom can combine either with four univalent atoms or groups or with the equivalent number of groups of other valencies. The four valencies are often represented conventionally by four bonds

FIG. 35.

(Fig. 35). Marsh gas and its chlorine substitution products will then be represented graphically as follows :—

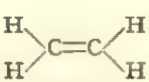


Methane. Methyl chloride. Methylene dichloride. Chloroform. Carbon tetrachloride.

Similarly carbon dioxide and hydrocyanic acid are written thus :

O=C=O H—C≡N

By means of single bonds between carbon atoms we are able to account for the existence of all the members of the paraffin family (Chapter V), and by using double or triple bonds to denote the special character of the so-called unsaturated compounds (Chapter XVII).

 and H—C≡C—H

Ethylene. Acetylene.

We shall see presently (Chapters VII and XXIII) that these plane formulae do not give a correct idea of the arrangement of the atoms in the molecule, which though small has three dimensions, but they can be used provisionally.

Classification.—It is desirable to have a system of classification based on similarity of constitution and chemical properties.

Chemical properties are compared by means of reagents. We can recognise the existence of several families of compounds. Three such families are represented by the paraffins, the alcohols, and the acids of the formic acid family.

PARAFFINS.

Formula.	Name.	Boiling-point.
CH_4	Marsh gas, or Methane	$-164°$
C_2H_6	Ethane	$-89°$
C_3H_8	Propane	$-45°$
C_4H_{10}	Butane	$+1°$
C_5H_{12}	Pentane	$+38°$
	etc.	

ALCOHOLS.

CH_4O	Methyl alcohol	66°
C_2H_6O	Ethyl alcohol	78°
C_3H_8O	Propyl alcohol	97°
$C_4H_{10}O$	Butyl alcohol	117°
$C_5H_{12}O$	Amyl alcohol	138°
	etc.	

ACIDS

CH_2O_2	Formic acid	101°
$C_2H_4O_2$	Acetic acid	118°
$C_3H_6O_2$	Propionic acid	141°
$C_4H_8O_2$	Butyric acid	162°
$C_5H_{10}O_2$	Valeric acid	185°
	etc.	

The members of the first group, the paraffins, are indifferent to most reagents; those of the second, the alcohols, readily undergo chemical change; whilst the last group, "the acids," as their name implies, are acids and form salts. Although the chemical behaviour of each family is the same, the physical properties, boiling-point, specific gravity, etc., vary from member to member. With increasing molecular weight, the boiling-point rises. It is customary to find the simplest member of a family represented by a gas or by a low-boiling liquid, the one with the largest molecule by a solid. In the case of the paraffins, the first four members are gases at the ordinary temperature, then follows a series of liquids, and at the bottom of the list we find those solids of which paraffin-wax is composed (p. 56).

Homologous Series.—It will be further observed that each member of a family differs from that which precedes or follows it by the same number of carbon and hydrogen atoms, viz. CH_2. The explanation of this will be given later. It is only necessary at present to state that families which fulfil the conditions just set forth were named by Gerhardt *homologous series.* A homologous series may therefore be defined as a family of chemically related compounds, the composition of which varies from member to member by one atom of carbon and two atoms of hydrogen. The three series of homologues which have been selected for illustration are by no means the only representatives; the number of such series is in fact very large, and each will be considered in its turn.

The advantage of such a grouping will now be obvious, for it will only be necessary to describe the chemical characteristics of one member, when that of the whole series of homologues may be inferred.

Reagents employed in Organic Chemistry.—The following are the most important reagents used in organic chemistry :—

OXIDISING AGENTS.—(1) Nitric acid (dilute and strong)—

$$2HNO_3 = 2NO + H_2O + 3O.$$

(2) Potassium permanganate in acid or alkaline solution—

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$
$$2KMnO_4 + H_2O = 2KOH + 2MnO_2 + 3O.$$

(3) Potassium dichromate and sulphuric acid—

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

(4) Chromium trioxide and glacial acetic acid—

$$2CrO_3 + 6C_2H_4O_2 = Cr_2(C_2H_3O_2)_6 + 3H_2O + 3O.$$

The use of a reagent in an organic solvent, like acetic acid, is of advantage on account of the solubility of organic substances in such solvents.

Hydrogen peroxide in presence of traces of ferrous salt (Fenton's reagent), ozone, bromine in presence of an alkali, selenium oxide (SeO_2) and electrolysis of aqueous solutions in which the substance is in contact with the positive electrode are also used occasionally.

REDUCING AGENTS.—These may be divided into acid, neutral and alkaline reducing agents.

Among the *acid reducing agents* are :—

(1) Hydriodic acid—

$$2HI = I_2 + H_2.$$

(2) Stannous chloride and strong hydrochloric acid—

$$SnCl_2 + 2HCl = SnCl_4 + H_2.$$

(3) Tin or iron and hydrochloric acid—

$$Sn + 4HCl = SnCl_4 + 2H_2.$$

(4) Zinc dust and glacial acetic acid—

$$Zn + 2C_2H_4O_2 = Zn(C_2H_3O_2)_2 + H_2.$$

Neutral reducing agents are :—

(1) The zinc-copper or aluminium-mercury couple—

$$ZnCu + 2H_2O = Zn(OH)_2 + Cu + H_2.$$
$$2AlHg + 6H_2O = 2Al(OH)_3 + Hg + 3H_2.$$

(2) Zinc dust and water—

$$Zn + 2H_2O = Zn(OH)_2 + H_2.$$

(3) Hydrogen in presence of finely divided nickel or copper-chromium oxide reduces many organic compounds at temperatures which vary according to the nature of the substance. The former method was discovered by Sabatier and Senderens. Hydrogen in presence of colloidal palladium and platinum, alone or deposited on charcoal or other inert substance, has a strong reducing action on substances dissolved or suspended in water or other solvent. Electrolytic hydrogen evolved at the negative electrode made of lead or cadmium is another important reducing agent.

Alkaline reducing agents are :—

(1) Sodium amalgam with alcohol or water—

$$2NaHg + 2H_2O = 2NaOH + Hg + H_2.$$

(2) Sodium methylate—

$$CH_3ONa + O = \underset{\text{Sodium Formate.}}{HCO_2Na} + H_2$$

(3) Zinc dust and caustic soda—

$$Zn + 2NaOH = Zn(ONa)_2 + H_2.$$

(4) Hydrogen sulphide in presence of ammonia (ammonium sulphide). Its action depends on the liberation of hydrogen and deposition of sulphur.

$$H_2S = H_2 + S.$$

THE HALOGENS.—The action of chlorine and bromine is in some cases promoted by light, and by the presence of small quantities of certain metals and their salts, such as iron and aluminium, the chloride or bromide of iron and antimony, also by sulphur and iodine. Such substances are called "halogen carriers," and their action is not fully understood. The chlorides and bromides of phosphorus are also frequently used for introducing chlorine and bromine into organic compounds, especially in place of oxygen or the hydroxyl (OH) group.

Dehydrating Agents.—These agents are of two kinds. One kind is employed for removing moisture from organic liquids. The common reagents for this purpose are fused calcium chloride, potassium carbonate, quicklime, or anhydrous magnesium or sodium sulphate. Another class of dehydrating agents is used to remove the *elements* of water from organic substances, thereby converting them into new compounds. The most useful substances of this class are concentrated sulphuric acid, phosphorus pentoxide, and fused zinc chloride.

Aliphatic, Aromatic, and Heterocyclic Series.—For convenience, organic compounds are grouped into three main series. The **aliphatic** (ἄλειφαρ, fat) series comprises not only fatty acids, but a large number of naturally related open-chain compounds of many types, such as methane, alcohol, formic acid, formaldehyde, ethylene, acetylene, together with their homologues and other related compounds. Benzene, on the other hand, forms the natural starting point of a group of cyclic compounds which are very numerous, and are called **aromatic.** It should be noted, however, that some cyclic compounds, the *naphthenes* (p. 256), are aliphatic in character. There is a third great series of compounds, the **heterocyclic** series (ἕτερος, other, different), consisting of cyclic compounds in which the rings are not entirely made up of carbon atoms.

Nomenclature.—Although many organic compounds are known by common names, which have long been established, they are vastly outnumbered by others. For these *official names* are used, which are derived from rules decreed by an International Committee, which seeks to standardise the nomenclature.

Questions on Chapter IV

1. Upon what system is the classification of organic compounds based? What special object does this classification serve?
2. Give a list of three of each of the following reagents: (i) oxidising; (ii) reducing; (iii) dehydrating agents; and describe their action by equations where possible.
3. What is meant by "homologous series"? Give an example.
4. Give examples of acid, neutral and alkaline reducing agents.
5. What substances are used as "halogen carriers"?

PART I

ALIPHATIC COMPOUNDS

CHAPTER V

PARAFFINS, OR SATURATED HYDROCARBONS

We shall begin with a study of the paraffins or saturated hydrocarbons, because they have a simple composition. They contain only carbon and hydrogen, being termed therefore *hydrocarbons.* They occur in Nature in large quantities, and they form, moreover, the natural starting-point for the whole of the aliphatic group of compounds. Table III., on the following page, contains a list of the paraffins, with their formulæ, melting-points, boiling-points, and specific gravities.

Nomenclature.—The names of the first four members are derived from those of the alcohols containing the same number of carbon atoms, "methyl," "ethyl," "propyl," and "butyl"; the remainder are indicated by the Greek numeral corresponding to the number of carbon atoms present. The names of all the paraffins terminate in "*ane.*" Several members, it will be observed, are represented by two or more substances. These have the same molecular formula, but a different grouping of their atoms. They are therefore **isomeric** with one another, and are termed **isomers** or **isomerides.** The difference in atomic arrangement will be discussed later (pp. 74, 75).

The paraffins are formed by the natural process of decay of vegetable and animal matter (see p. 67).

Paraffins are also formed by the decomposition of animal and vegetable matter by heat, as in the destructive distillation of wood and coal; but the most plentiful source is the petroleum wells.

The most important localities in which petroleum is found are the United States, Mexico, Russia, Persia, and the Dutch East Indies. A certain quantity is also produced in India and Canada.

TABLE III

PARAFFINS—C_nH_{2n+2}

Formula.	Name.	Melting point.	Boiling point.	Specific gravity.
CH_4 .	Methane	−186	−164°	·415 At b.p.
C_2H_6 .	Ethane	−172	− 90°	·446 At 0°
C_3H_8 .	Propane		− 38°	·536
C_4H_{10}	Normal Butane		+ 1°	·600
	Isobutane		− 17°	—
C_5H_{12}	Normal Pentane		+ 36°	·633 At 15°
	Dimethylethylmethane or Isopentane		+ 28°	·627
	Tetramethylmethane or Neopentane		+ 10°	
C_6H_{14}	Normal Hexane		69°	·677 At 0°
	Dimethylisopropylmethane		58°	·679
	Dimethylpropylmethane .		62°	·672
	Methyldiethylmethane .		64°	
	Trimethylethylmethane .		48°	
C_7H_{16}	Heptane		98°	·700 At 0°
	Isoheptane		90°	·697
C_8H_{18}	Octane		125°	·718
C_9H_{20}	Nonane		150°	·733
$C_{10}H_{22}$	Decane		173°	·745
$C_{11}H_{24}$	Undecane		195°	·774 At the melting point.
$C_{12}H_{26}$	Dodecane		214°	·773
$C_{13}H_{28}$	Tridecane		234°	·775
$C_{14}H_{30}$	Tetradecane		252°	·775
$C_{15}H_{32}$	Pentadecane		270°	·776
$C_{16}H_{34}$	Hexadecane	18°	287°	·775
$C_{17}H_{36}$	Heptadecane	22°	303°	·777
$C_{18}H_{38}$	Octadecane	28°	317°	·777
$C_{19}H_{40}$	Nonadecane	32°	330°	·777
$C_{20}H_{42}$	Eicosane	37°	205° At 15 mm. pressure.	·778
$C_{21}H_{44}$	Heneicosane	40°	215°	·778
$C_{22}H_{46}$	Docosane	44°	224°	·778
$C_{23}H_{48}$	Tricosane	48°	234°	·779
$C_{24}H_{50}$	Tetracosane	51°	243°	·779
$C_{27}H_{56}$	Heptacosane	60°	270°	·780
$C_{31}H_{64}$	Hentriacontane	68°	302°	·781
$C_{32}H_{66}$	Dotriacontane	70°	310°	·781
$C_{35}H_{72}$	Pentatriacontane	75°	331°	·782

The world's output of petroleum is about 250 million metric tons,[1] to which the United States contribute about 70 per cent.

The Petroleum and Paraffin Industry.—The oil deposits found in different parts of the world yield what is known as petroleum, earth oil, rock oil, or mineral oil. The origin of the oil has been variously attributed to the action of steam on the iron carbide of subterraneous mineral deposits (Mendelejeff), which acts like water on aluminium carbide (see p. 68), and to the decomposition at high temperatures and under pressure of the remains of marine life. The latter view is supported by the experiments of Engler, who heated the blubber of fish under pressure, and obtained a quantity of paraffins. It is an interesting fact that when acetylene mixed with hydrogen is passed over finely divided nickel at about 200° a mixture of hydrocarbons resembling petroleum is produced (Sabatier). The petroleum is found in sand or conglomerate known as "sand rocks," and is obtained by boring and pumping.

AMERICAN PETROLEUM was discovered in 1859 by Colonel Drake, in Pennsylvania. It has since been found in Ohio, Colorado, California, Texas, and other places. The oil is obtained by boring down to the oil-bearing stratum and pumping. Large quantities of natural gas are at the same time emitted, which is either liquefied or used as a source of heat and light. The crude oil from the Pennsylvanian oil fields is carried to the sea coast along iron pipes, some of which are 300 miles long. Here the oil is fractionally distilled in large iron stills and purified. It is divided into the following fractions, which are recognised in the trade by various names :—

Name.	Fraction.	Specific gravity at 15°.	Constituents.	Percentage.
Cymogene	B.p. 0°	0·636	—	16·5
Rhigolene	18°		—	
Petroleum ether, or Gasoline	40°–90°	0·642–0·648	C_5H_{12}—C_6H_{14}	
Petroleum naphtha, or Ligroin	90°–120°	0·648–0·692	C_6H_{14}—C_8H_{18}	
Petroleum benzine,[2] or Benzoline	120°–150°	0·692–0·730	C_8H_{18}—C_9H_{20}	
Kerosene, Photogene, or Burning oil	150°–300°	0·790–0·810	$C_{10}H_{22}$—$C_{16}H_{34}$	54·0
Lubricating oil	—	—	—	17·5
Vaseline	—	—	—	—
Solid paraffin, or paraffin wax	M.p. 45°–65°	—	—	2·0

[1] A metric ton = 1000 kilos. = 2205 lbs., or 0·984 ordinary ton (2240 lbs.).

[2] Not to be confused with coal-tar *benzene*.

Cymogen is liquefied by pressure, and by its rapid evaporation lowers the temperature and is used for making ice; *rhigolene* is used in surgery to produce local insensibility by freezing; *petroleum ether* and *ligroin* are used for dissolving and extracting fats and oils; and *benzine* is employed for a similar purpose in dry cleaning. *Petrol*, which is used in internal combustion engines, has a boiling-point of 70–120° C. and a specific gravity of 0·700–0·760, consisting of paraffins C_6H_{14}–C_8H_{18}.

The *kerosene* is purified after distillation by agitating it with concentrated sulphuric acid and afterwards with caustic soda solution and redistilling. The quantity of the more volatile fractions may be increased by "cracking," that is, by heating to a high temperature the portions of higher boiling-point, which then break up into products of lower boiling-point. The process of cracking is carried out under pressure and also occasionally in presence of hydrogen and a metallic catalyst to prevent the formation of unsaturated hydrocarbons. The annual output of the United States is nearly 100 million metric tons.

The American petroleum does not consist exclusively of paraffins. There appear to be also present small quantities of hydrocarbons of the benzene series (p. 385), and substances termed *naphthenes* of the formula C_nH_{2n} (p. 256).

Russian Petroleum is found in and around the town of Baku, which stands on the peninsula of Apsheron on the Caspian Sea. The so-called "eternal fires of Baku" attracted the fire-worshippers as early as 600 B.C. Marco Polo described them, and an English traveller, Hanway, in 1754, gave an account of the inflammable vapour with which the ground in the district was saturated.

Systematic working for oil began in 1813, but the output was restricted by Government monopoly, which was abolished in 1872, and in the following year Nobel Brothers started their immense works. The total quantity of oil produced annually is about 2250 million gallons. The oil differs from American oil, both in its character and in the conditions under which it occurs. It is contained under great pressure, so that in sinking the bore-holes, the oil frequently is driven out to an enormous height. The great Droojba well spouted for four months an oil column from 100 to 300 feet high, which ran to waste, and caused a loss of about 100 million gallons. Occasionally the wells take fire and burn for many weeks. The oil is distilled and purified like the American

petroleum. Russian oil contains less of the lower-boiling portions than American oil. It consists on the average of—

30 per cent. illuminating oil.
30 per cent. lubricating oil.
35 „ solar oil, or ostatki, a heavy oil used for fuel.

The illuminating oil has a higher specific gravity than the American oil (0·820–0·825) in consequence of the presence of a large proportion of *naphthenes* (p. 256).

Paraffin Industry in Scotland.—The origin of the paraffin industry is due to James Young, who discovered a petroleum spring in Derbyshire in 1848; but the spring shortly afterwards becoming exhausted, he looked about for fresh sources of supply, and found that a bituminous shale occurring in Scotland—the celebrated Torbanehill mineral—would yield paraffin oil on distillation.

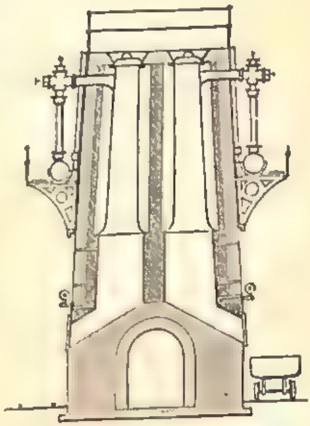


Fig. 36.—Shale retort.

The shale is distilled by a continuous process in long vertical retorts, the upper portion of which is of iron and the lower of fireclay, the fresh shale being supplied through the top, and the spent shale withdrawn at the bottom. Fig. 36 represents a vertical section of a retort. The inflammable gases, ammonia, and oil pass into the hydraulic main, and thence into coolers where the tar is deposited, the ammonia being collected as in a gas-works, and the inflammable gases used for fuel and illumination. About 30 gallons of oil are obtained from 1 ton of shale. The viscid and tarry-looking oil is redistilled to remove the portions of lower boiling-point, and purified by treatment, first with strong sulphuric acid, and then with caustic soda. It is again distilled, and the distillate is separated into—

Naphtha.
Burning, or paraffin oil.
Light mineral oil.
Residue.

The residue is treated for paraffin-wax or *scale*. It is first frozen, when it becomes semi-solid, and then passed through a filter press. The filtrate is a viscid liquid, and is used as lubricating oil. The scale is pressed hot to remove adhering oil, and finally *sweated*. This process consists in placing the wax in large cakes on a sloping table in a heated chamber, whereby the lower melting portions run away, leaving behind a much firmer material. The wax is a mixture of paraffins, and melts between 45° and 70°. It is chiefly used in the manufacture of candles. About one-half of the 40,000 tons of paraffin wax produced annually is derived from Scotch shale.

A new source of liquid fuel resembling petroleum is obtained by submitting finely divided coal to the action of hydrogen at a temperature of 400–450° and at a pressure of 100–200 atmospheres in presence of various metallic or metallic oxide catalysts. The product is stated to consist of about one-fifth motor spirit, one-fifth "Diesel" oil, and the remainder lubricating oil and pitch (*Bergius* process).

The substance known as *Ozokerite* is found in mines in Galicia, and consists mainly of paraffins. It is used for medical purposes and a preparation of it, resembling beeswax, is sold under the name of *cerasine*.

Liquid Fuel (*i.e.* the higher boiling (heavy) oils from petroleum, shale, and coal-tar) is gradually displacing solid fuel for steam-raising. It has many advantages over coal. It has a higher calorific value (about 19,000 B.Th.U.[1]) compared with coal (about 12,500 B.Th.U.). When used on board ship it is stored with greater safety and with economy in space and labour. It is easily handled, makes no clinker and can be pumped directly into tanks without the dirt attending the loading of coal.

The liquid fuel which is used in internal combustion engines may be divided into two classes, viz., heavy oils with low vapour pressure, which are ignited with air by compression in Diesel engines, and those with high vapour pressure, petrol, benzene (p. 388), and alcohol (p. 102), or mixtures of these, which are used with carburettors in motor engines.

[1] A Calorie (Cal.) is the heat required to raise 1 kilo. of water 1° C.; a British Thermal Unit (B.Th.U.) to raise 1 lb. of water 1° F.

1 B.Th.U. = 0·252 Cals.; 1 Cal. = 3·96 B.Th.U.

The following table[1] gives the general properties of these three liquids:

	Petrol.	Commercial 90% benzol.	Methylated spirit (alcohol).
Specific gravity	0·680–0·760	0·883	0·820
Boiling-point	60°–150° C.	80°–120° C.	80°–110° C.
Specific heat	0·470	0·416	0·615
Heat of vaporisation (calories)	86	94·35	203
Calorific value, B.Th.U. per lb. net	18·450	17·100	10·350
Air required, cb. ft. per lb. at 60° (theoretical)	197	175	113·5
Calorific value of 1 cb. ft. of above mixture of air and vapour	103	105	97·5
Compression limit in lbs.	70	Slightly above petrol	About 200

Benzene can be used with the same efficiency as petrol, but is usually mixed with the latter. Alcohol has the advantage over petrol and benzene by reason of its lower volatility and higher flash-point, and is therefore less readily ignited. Although it has a lower calorific value than the other two liquids, the actual consumption for a given power is not much higher. The thermal efficiency being roughly proportional to the compression, the higher compression limit (*i.e.* without danger of pre-ignition or back-firing) gives it an advantage, so that difference in calorific value is largely eliminated. Owing to its high heat of vaporisation, starting the engine may be difficult, unless the liquid is warm or benzene or petrol added.

Petroleum and Motor Oils.—The crude oil which is first obtained contains much gas, of which the largest proportion is the relatively unprofitable methane (p. 67). Simple distillation gives only about 20 per cent. of motor spirit, containing both normal and iso-paraffins. Normal paraffins are in general very much less efficient as fuels in the internal-combustion engine than iso-paraffins, of which the most important is iso-octane owing to its freedom from "knock" (p. 244). Knocking is caused by the premature detonation of the air–fuel mixture. The octane-rating or octane number of a fuel depends upon the percentage of iso-octane which it contains. The demand for a fuel with a high octane

[1] This table is in part reproduced from *Fuel*, by J. S. S. Brame: E. Arnold, 1924.

number has become so great since the development of the modern internal-combustion engine with its high compression ratio that its yield from simple distillation has had to be greatly supplemented by means of the pyrolysis or "cracking" (p. 58) of both simple and complex fractions. Cracking means thermal and catalytic decomposition and yields not only motor spirit but also olefines, which have become of increasing importance in the production of synthetic rubber, plastics, and other useful materials. Also under high pressure catalytic hydrogenation can be made to increase the yield of petrol and even to produce aromatic hydrocarbons, which are used in the manufacture of high explosives and dyestuffs. The less-volatile fraction from the distillation of crude petroleum contains lubricating oils and waxes as well as asphalt. The former are freed from olefines by solvent extraction or by hydrogenation under pressure. Among them are ethylene and propylene (p. 247). From ethylene we can get alcohol (p. 112) and glycol (p. 88), a useful anti-freeze substance, and from propylene we get iso-propyl alcohol, acetone, and glycerol. The rather refractory hydrocarbon methane to which reference has been made can now be converted by pyrolysis to acetylene (p. 257), which has become the starting point in many useful syntheses.

In consequence of the large consumption of paraffin oil for lamps, and the danger of explosion from the use of too volatile an oil, which may form an explosive mixture with the air inside the reservoir, the Government insist upon a certain standard quality, which is determined by the "flashing-point." The standard apparatus is shown in Fig. 39, and the method is known as Abel's test. The apparatus consists of a cylindrical metal cup, surmounted by a metal cover, holding a slide, which opens or closes apertures in the cover. In moving the slide so as to uncover the central hole, an oscillating lamp is caught by a pin fixed in the slide, and tilted in such a way as to bring the nozzle just below the surface of the lid. When the slide is pushed back so as to cover the hole, the lamp returns to its original position. The vessel is charged to a certain height with the oil to be tested, and a thermometer inserted through the cover, the bulb of which is immersed in the oil. The vessel is heated in a specially constructed water-bath, and as the temperature of the oil rises, the slide is occasionally withdrawn, so

as to expose the interior of the cup to the jet of flame. When the vapour ignites, the temperature is observed, and this is the flashing-point.

The lowest flashing-point by Abel's apparatus permitted by the Board of Trade is 73° F., but it is now generally recognised that this minimum has been fixed too low.

One of the most common sources of danger in the use of oil lamps is that arising from the burning down of a loosely-fitting and short wick, the lower end of which is not immersed in the oil. Such a wick may smoulder within the reservoir, and occasionally fire an explosive mixture of paraffin vapour and air. This danger is easily avoided by examining the wick occasionally, and renewing it before it becomes too short.

EXPT. 10.—Pour a few c.c. of paraffin oil into a large flask with a wide neck, heat the oil strongly, and blow a little air through with a bellows. If a piece of lighted wick, or roll of paper, be dropped in a vigorous explosion occurs.

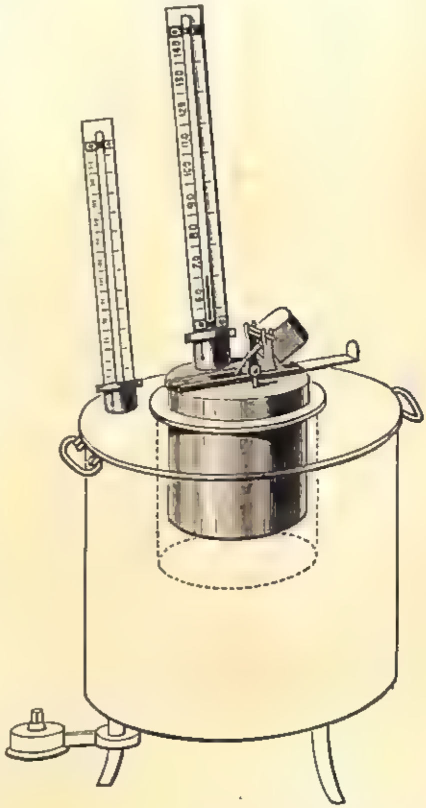


FIG. 39.—The Abel flashing-point apparatus.

Physical and Chemical Properties of Paraffins.—The paraffins are specifically lighter than water, and being insoluble, they float on water. The lower and more volatile members have a peculiar and not unpleasant smell.

Strong and dilute mineral acids have little action on the paraffins,

and they are scarcely attacked by oxidising agents under ordinary conditions; but at higher temperatures and in presence of a metallic catalyst they may be converted into fatty acids (see p. 146). Such methods have been introduced for converting the higher paraffins and paraffin wax into acids, which can be utilised for various commercial purposes, as in the manufacture of candles, soap, etc. It is owing to this indifference to most reagents that the term paraffin (*parum*, little; *affinis*, affinity) has been applied.

Fuming sulphuric acid and dilute nitric acid under pressure have been found to react with some of the paraffins, the former giving sulphonic acids, and the latter nitro-compounds (p. 410).

Addition and Substitution.—When chlorine reacts with carbon monoxide, either in sunlight or in the presence of a catalyst, the resulting product, carbonyl chloride or phosgene is formed **additively** or by direct combination of two molecules.

$$CO + Cl_2 = \underset{\text{Carbonyl chloride.}}{COCl_2.}$$

On the other hand chlorine and bromine react with paraffins only by **substitution,** hydrogen chloride or bromide being evolved at the same time. The reaction proceeds violently with the gaseous paraffins but less rapidly with higher members. Substitution is greatly accelerated by sunlight. Iodine however does not react in this way.

The action of chlorine on methane is represented as follows—

$$CH_4 + Cl_2 = \underset{\substack{\text{Monochloromethane,}\\ \text{or Methyl chloride,}}}{CH_3Cl} + HCl,$$

an atom of hydrogen being replaced by an atom of chlorine.

Expt. 11.—This action of chlorine on the paraffins may be illustrated by taking a long, wide glass tube closed at one end and filled with strong brine. It is inverted in a bath of brine, and sufficient chlorine is introduced to fill it one-third full. This is marked with a strip of paper. An equal volume of marsh-gas is then passed into the tube, and the volume indicated by a fresh strip of paper. The apparatus is shown in Fig. 40. The mixture is left in diffused light (bright sunlight will cause an explosion). After several hours the mixed gases will occupy about one-half the original volume. As equal volumes of the two gases contain the same number of molecules, the equation may be written—

$$\underset{\substack{\text{1 vol.,}\\ \text{or 1 mol.}}}{CH_4} + \underset{\substack{\text{1 vol.,}\\ \text{or 1 mol.}}}{Cl_2} = \underset{\substack{\text{1 vol.,}\\ \text{or 1 mol.}}}{HCl} + \underset{\substack{\text{1 vol.,}\\ \text{or 1 mol.}}}{CH_3Cl}$$

As the hydrochloric acid is absorbed by the brine, only the methyl chloride remains, which occupies half the original volume.

FIG. 40.—Action of chlorine on marsh-gas.

Substances which, like the paraffins, lose hydrogen in the form of hydracid when they enter into combination with the halogens, are termed **saturated** compounds, and the process of replacement of hydrogen by a halogen is termed **substitution.** The products obtained by substitution are known as **substitution products.** The term substitution is not confined to the exchange of hydrogen for chlorine or bromine. The exchange of hydrogen for oxygen or any other element, or of one group of elements for another, is sometimes termed substitution. The process has now lost its original theoretical significance. It played an important part in the overthrow of the dualistic theory.[1]

This process of substitution effected by the action of chlorine on the paraffins will continue, provided enough chlorine is present, until the whole of the hydrogen is replaced by chlorine. For example, by the further action of chlorine on methyl chloride, the following products are formed :—

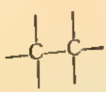
$$CH_3Cl + Cl_2 = HCl + \underset{\substack{\text{Dichloromethane, or} \\ \text{Methylene chloride.}}}{CH_2Cl_2}$$

$$CH_2Cl_2 + Cl_2 = HCl + \underset{\substack{\text{Trichloromethane,} \\ \text{or Chloroform.}}}{CHCl_3}$$

$$CHCl_3 + Cl_2 = HCl + \underset{\substack{\text{Tetrachloromethane, or} \\ \text{Carbon tetrachloride.}}}{CCl_4}$$

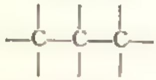
We have now to explain the existence of homologous series and to discuss the cause which determines the constant difference of CH_2 between each successive member of the series.

Linking of Carbon Atoms.—Let us take the case of two atoms of carbon linked together.



[1] *Vide* E. von Meyer, *History of Chemistry* (Macmillan).

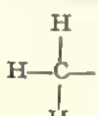
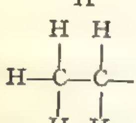
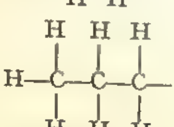
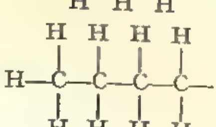
If these bonds are united to hydrogen atoms, the formula C_2H_6 is obtained, which is that of the second member of the paraffin series. Three carbon atoms utilise 4 bonds in effecting a linkage between themselves, leaving 8 bonds free. Hence the third member of the paraffins is represented by the formula C_3H_8—



If we continue to build up chains of carbon atoms on this principle, we shall find that each end carbon atom of the chain has three available bonds, whereas each of the middle carbon atoms possesses only two. If, therefore, n is the number of carbon atoms present in the compound, there will be $2n$ bonds available for each carbon atom and 2 extra for the two end carbon atoms, making $2n + 2$ available bonds. If, as in the paraffins, these available bonds are attached to hydrogen, the general formula for the paraffins will be C_nH_{2n+2}.

The following univalent groups, which enter into the structure of many organic compounds, are denoted by special names, the significance of which will be explained later :

Alkyl Radicals.

Formula.	Name.	Abbreviation.
	CH_3' Methyl	Me
	C_2H_5' Ethyl	Et
	C_3H_7' Propyl	Pr
	C_4H_9' Butyl	Bu

A characteristic feature of the paraffin series is that all the linkages between carbon atoms are *single* bonds, so that the valencies are fully satisfied or **saturated,** and chemical reaction can therefore only take place by substitution. We shall see presently that the chains are sometimes continuous and sometimes branched, but in no case is it correct to speak of a *straight* chain, for the chains must be bent or coiled in some way. Although the molecule of methane is frequently formulated thus—

$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

it is highly improbable that the hydrogen atoms lie in a circle round the carbon atom. It is much more probable that they are grouped symmetrically in the form of a solid model.

Having now reviewed the chief sources and principal properties of the paraffin family, we will consider in greater detail the characters of a few of the more important members.

Methane, marsh-gas, or **fire-damp,** CH_4, is the only hydrocarbon containing one atom of carbon. It is found in the gases from oil wells and rising from stagnant water where it is produced by the action of organisms on the cellulose of woody fibre. The reaction may be represented by the following equation:

$$\underset{\text{Cellulose.}}{(C_6H_{10}O_5)_n} + nH_2O = (3CO_2)_n + \underset{\text{Marsh-gas.}}{(3CH_4)_n}$$

It is frequently present in coal-pits, especially during a sudden fall in atmospheric pressure, when it diffuses from crevices and old workings. It is also formed by the distillation of coal, and forms about 40 per cent. by volume of coal-gas. It is an interesting fact that methane can be obtained by the direct union of carbon and hydrogen at 1200°, or by means of an electrical discharge between carbon poles in an atmosphere of hydrogen.

Methane can also be obtained by passing carbon monoxide, or dioxide, mixed with hydrogen, over finely-divided nickel heated to about 300°. The method is being utilised for its commercial production (Sabatier–Senderens' method).

$$CO + 3H_2 = \underset{\text{Methane.}}{CH_4} + H_2O.$$

It is usually prepared by heating together fused potassium or sodium acetate with soda-lime—

$$\underset{\text{Sodium acetate.}}{C_2H_3O_2Na} + NaOH = \underset{\text{Methane.}}{CH_4} + Na_2CO_3.$$

This reaction has an important bearing on the structure of acetic acid, and will be referred to again (p. 149).

EXPT. 13. *Preparation of Methane.*—Powdered potassium acetate (20–30 grams) is mixed with three times its weight of soda-lime. The

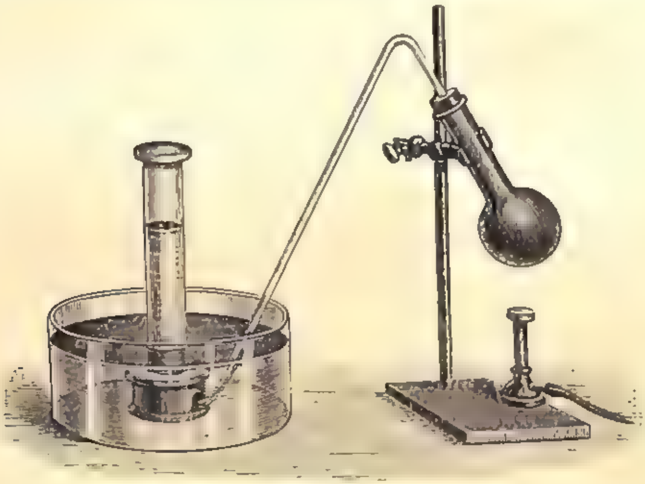


FIG. 41.—Preparation of Marsh-gas from Potassium acetate.

mixture is introduced into a glass or copper flask which is inclined as in Fig. 41. The flask is closed with a cork, into which a delivery-tube is inserted. The flask is strongly heated, and after the air has been expelled the gas is collected in a gas bottle over water, and the bottle, when full, is closed with a stopper. The gas is very far from pure, and burns with a luminous flame. To remove the luminous hydrocarbons the vaselined stopper is raised slightly and a little concentrated sulphuric acid is poured in quickly and rinsed round, followed by some fuming sulphuric acid, and the bottle is quickly closed and left for an hour. The gas then burns with a non-luminous flame.

Methane can be conveniently prepared by the action of water on aluminium carbide—

$$Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3.$$

Expt. 14.—The aluminium carbide is placed in a shallow layer over a layer of sand in a large flask, furnished with a rubber cork having two holes and carrying a dropping funnel and delivery tube. Dilute hydrochloric acid is allowed to drop slowly on to the carbide, whereupon methane is evolved, and, after expelling the air, may be collected over water. The gas may be liquefied, if liquid air is available, by removing any carbon dioxide by passing the gas through a strong solution of caustic potash, drying it through calcium chloride and then passing it through a narrow U-tube, also furnished at the exit end with a drying tube, and cooled in liquid air.

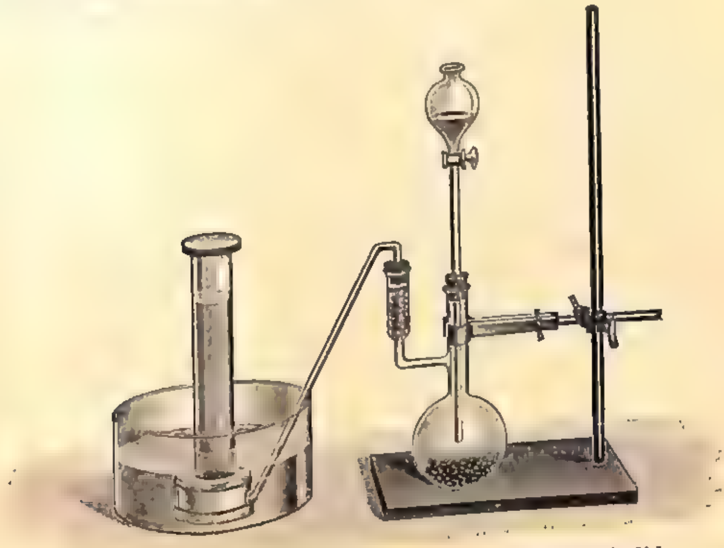


Fig. 42.—Preparation of Marsh-gas from Methyl iodide.

The gas is obtained in a pure state by the action of the zinc-copper or mercury-aluminium couple on methyl iodide in presence of water or alcohol. The couples act on the water or alcohol, and liberate hydrogen, which reduces the methyl iodide—

$$\underset{\text{Methyl iodide.}}{CH_3}\boxed{I + H}H = CH_4 + HI.$$

Expt. 15. *Preparation of Methane: another method.*—Fit up an apparatus as shown in Fig. 42.

It consists of a flask through the neck of which a tap-funnel is fixed. The flask is fitted with a horizontal side-tube to which a wider vertical

tube is fused. The flask and vertical side-tube are then partly filled with the zinc-copper or aluminium-mercury couple. The zinc-copper couple is prepared by immersing granulated zinc (20–30 grams) in a solution of copper sulphate until a film of metallic copper covers the surface of the zinc. The couple is washed with water, and the water removed by pouring fresh alcohol on and off two or three times. This can be done conveniently in a wide-necked tap-funnel. The aluminium-mercury couple is prepared by immersing little rolls of sheet aluminium in mercuric chloride solution until a film of mercury covers the surface of the aluminium which is washed as described above. The couple is then placed in the flask and side-tube and 50 c.c. of methyl alcohol containing 2 drops of dilute sulphuric acid (if the zinc-copper couple is used) are poured in. The side-tube containing the couple is closed by a cork and delivery-tube and the flask, if necessary, cooled in water. The methyl iodide is added gradually from the tap-funnel. After driving out the air, the gas is collected over water.

The hydrogen is supplied by the methyl alcohol, and in the case of the zinc-copper couple the reaction occurs according to the equation—

$$CH_3I + Zn + CH_3OH = Zn\begin{cases} I \\ OCH_3 \end{cases} + CH_4.$$

Zinc methoxyiodide.

Probably a similar reaction takes place in the case of the aluminium.

Methane is produced during the removal from coal-gas of the impurity carbon disulphide by catalytic reduction in the presence of nickel.

Properties of Methane.—Methane is a colourless gas, without smell. It condenses to a liquid at $-164°$ under a pressure of 760 millimetres. When the pressure is suddenly released, the liquid boils, and then solidifies, the temperature falling to $-186°$. The sp. gr. of liquid methane at 0° is 0·554. The gas burns with a non-luminous flame, and explodes violently when mixed with air or oxygen and fired. Methane shares the general properties of the paraffins in being unaffected by most reagents. Substitution takes place with chlorine and bromine, as already explained (p. 64).

Composition of Methane.—The simplest way of determining the composition of methane is to explode in a eudiometer a measured volume of the gas with an excess of air. The contraction in volume determines the quantity of hydrogen, and the further contraction

(on adding potash, to absorb the carbon dioxide) gives the amount of carbon—

$$\underset{\substack{1\text{ vol.,}\\ \text{or }1\text{ mol.}}}{CH_4} + \underset{\substack{2\text{ vols.,}\\ \text{or }2\text{ mols.,}}}{2O_2} = \underset{\substack{1\text{ vol.,}\\ \text{or }1\text{ mol.}}}{CO_2} + \underset{\substack{2\text{ vols.,}\\ \text{or }2\text{ mols.}}}{2H_2O}.$$

Now, water-vapour contains its own volume of hydrogen. If, therefore, for 1 volume of methane taken, 2 volumes of gas disappear after explosion, the diminution in volume corresponds to 2 volumes of hydrogen = 2 molecules or 4 atoms of hydrogen.

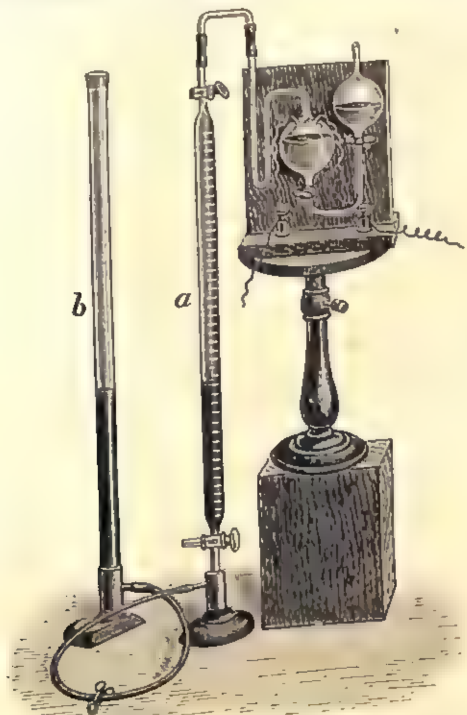


FIG. 43.—Hempel's apparatus.

In the same way, 1 volume or molecule of carbon dioxide contains 1 atom of carbon. As every volume of methane gives 1 volume of carbon dioxide, the formula of methane will be CH_4. By this method both the composition and molecular weight of methane are found without the weight of the constituents or the density of the gas being known.

Hempel's apparatus (Fig. 43) furnishes a rapid method for estimating the amount of methane and other paraffins in coal-gas, or other mixture of gases. It consists of two upright tubes, *a* and *b*, supported on stands, and connected below by rubber tubing. One of the tubes, *a*, is finished with two taps, and holds from tap to tap exactly 100 c.c., graduated in tenths of a c.c. The other tube, *b*, is filled with mercury. The coal-gas is introduced into the graduated tube by means of the lower three-way tap, and is allowed to stream through until the air is displaced. The top tap is closed, and the lower tap turned so that it places the two tubes *a* and *b* in communication. By letting in the mercury from the tube *b*, the gas is driven over into "pipettes," consisting of double bulbs containing various absorbents. In this way the different constituents of the coal-gas are in turn removed and measured by loss on the original volume, except hydrogen, marsh-gas, and nitrogen. A portion of this residue, consisting of these three gases, is then passed into the graduated limb of a similar apparatus. An excess of air is introduced and measured, and the mixture passed into an "explosion pipette," shown in Fig. 43, where it is fired by sparking through platinum terminals. The gas is then passed back into the graduated tube in which it was mixed with air and again measured, and from the diminution in volume the total volume of hydrogen is determined. By passing the gas into an absorption pipette containing potash, the carbon dioxide is removed, and this further loss of volume gives the quantity of carbon which is present as marsh-gas. The same method may be applied to other gaseous hydrocarbons.

Ethane, or *Dimethyl*, $CH_3{\cdot}CH_3$, occurs with methane in the gases from petroleum wells, and, like methane, it is formed in minute quantities by sparking carbon terminals in an atmosphere of hydrogen. It may be prepared by the action of zinc (Frankland and Kolbe) or sodium (Wurtz) on methyl iodide. The reaction is represented as follows :—

$$2CH_3I + Zn = CH_3{\cdot}CH_3 + ZnI_2$$

$$\underset{\text{Methyl iodide}}{2CH_3I} + 2Na = \underset{\text{Ethane}}{CH_3{\cdot}CH_3} + 2NaI$$

This condensation of the lower alkyl halides (p. 85) with sodium is difficult to carry out at the atmospheric pressure owing to their low boiling points, as the alkyl halide is apt to boil away without interacting with the sodium, but the reaction can be catalysed by the addition of acetonitrile (p. 224).

This process represents not only a general synthetic method by which many of the paraffins may be built up, but is one of great

theoretical importance. It affords strong evidence in support of the theory of the linking of carbon atoms. As the removal of an atom of iodine from each molecule of methyl iodide leaves one carbon bond free, it must be by this single residual bond that the carbon atoms are united.

As two methyl groups are represented as linked together, the hydrocarbon may be called *dimethyl*. Ethane is most readily prepared by the reduction of ethyl iodide with the zinc-copper couple, as in the preparation of methane—

$$C_2H_5I + H_2 = C_2H_6 + HI.$$

There are other methods of preparation, which will be referred to in subsequent chapters (pp. 240, 247).

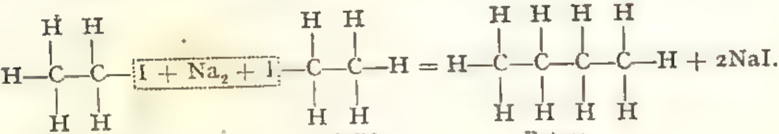
Ethane is a colourless gas which can be liquefied at 4° under a pressure of 46 atmospheres. It is acted upon by chlorine and bromine, the final products being *carbon hexachloride*, C_2Cl_6, and *carbon hexabromide*, C_2Br_6, both of which are colourless, crystalline solids.

Propane, or *Ethyl methyl*, $CH_3{\cdot}CH_2{\cdot}CH_3$, is also a constituent of petroleum gas. It may be prepared by the reduction of propyl iodide, C_3H_7I, with the zinc-copper couple, or by the action of sodium on a mixture of methyl iodide and ethyl iodide. Both ethane, C_2H_6, and butane, C_4H_{10}, are formed at the same time—

$$\underset{\text{Ethyl iodide.}}{CH_3{\cdot}CH_2}\boxed{I + Na_2 + I}\underset{\text{Methyl iodide.}}{CH_3} = \underset{\text{Propane.}}{CH_3{\cdot}CH_2{\cdot}CH_3} + 2NaI.$$

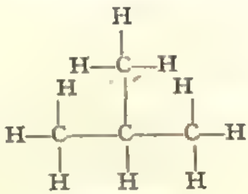
As in the case of ethane, the structure of propane is confirmed by this synthesis.

Butane, C_4H_{10}.—If reference is made to Table III. (p. 55), it will be noticed that there are two substances with the formula C_4H_{10}, viz. *normal butane* and *isobutane*. The two compounds are therefore isomeric. Their chief difference lies in their boiling-points, normal butane being liquid at + 1°, whereas isobutane can only be liquefied at the ordinary pressure at − 17°. Moreover, the products obtained from each by the action of chlorine and bromine have different properties. How is this difference to be accounted for? It is a question of atomic arrangement. The structure of normal butane is determined by synthesis from ethyl iodide and sodium, and has therefore a simple chain of carbon atoms—



Ethyl iodide. Ethyl iodide. Butane.

This substance may therefore be termed *diethyl*, $C_2H_5 \cdot C_2H_5$. We may consider the formula of normal butane to be derived from that of propane by the addition of a carbon atom, with its accompanying hydrogen atoms, to an end carbon atom of propane. But there is a second possible arrangement of 4 carbon atoms and 10 hydrogen atoms, forming, not a simple, but a branched chain, thus—

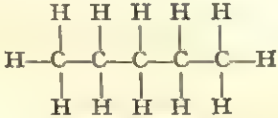


Isobutane.

This second formula may be derived from propane by attaching a fourth carbon atom to the middle carbon atom of propane. It represents a central carbon atom attached to 3 methyl groups, or methane in which 3 hydrogen atoms are replaced by 3 methyl groups. It may therefore be termed *trimethylmethane*, $CH(CH_3)_3$. The formula agrees with the synthesis of isobutane from tertiary butyl iodide by reduction (p. 86)—

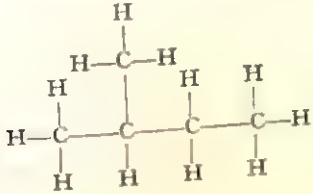
$$\underset{\text{Tertiary butyl iodide.}}{(CH_3)_3CI} + H_2 = \underset{\text{Isobutane.}}{(CH_3)_3CH} + HI$$

Pentane, C_5H_{12}.—This formula stands in Table III. (p. 55) for three compounds, which corresponds exactly with the theoretical number of combinations of 5 carbon atoms. One arrangement is produced by adding a fifth carbon atom to one of the end carbon atoms of normal butane—

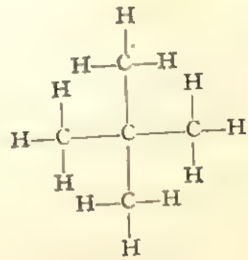


Normal Pentane.

This structure is present in normal pentane. Again, the additional carbon atom may be attached either to an end or middle carbon atom of isobutane, and in each case a different grouping will result—



Isopentane.



Neopentane.

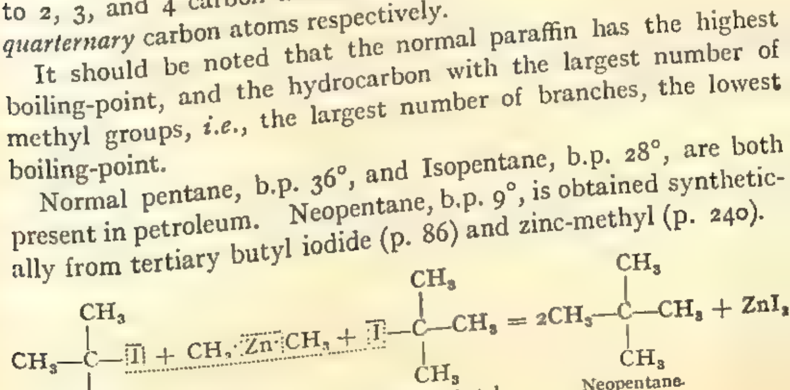
The first is called *isopentane*, or *dimethylethylmethane*, $C_2H_5 \cdot CH \cdot (CH_3)_2$; the second *neopentane*, or *tetramethylmethane*, $C(CH_3)_4$.

Normal, iso-, and neo-paraffins.—A *normal* paraffin represents an *unbranched* chain of carbon atoms, each intermediate carbon atom being linked to 2 others; an *iso-paraffin* has at least one carbon attached to 3 other carbon atoms, while a *neo-paraffin* has at least one carbon atom attached to 4 other carbon atoms.

A terminal carbon atom is only linked to *one* carbon atom, and is therefore called a *primary* carbon atom, those which are linked to 2, 3, and 4 carbon atoms being called *secondary*, *tertiary*, and *quarternary* carbon atoms respectively.

It should be noted that the normal paraffin has the highest boiling-point, and the hydrocarbon with the largest number of methyl groups, *i.e.*, the largest number of branches, the lowest boiling-point.

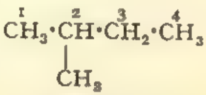
Normal pentane, b.p. 36°, and Isopentane, b.p. 28°, are both present in petroleum. Neopentane, b.p. 9°, is obtained synthetically from tertiary butyl iodide (p. 86) and zinc-methyl (p. 240).



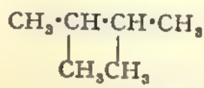
Tertiary butyl iodide. Zinc methyl. Tertiary butyl iodide. Neopentane.

Pentane, carefully fractionated from petroleum, is used in a lamp of special construction as a standard illuminant for determining the illuminating power of coal-gas, etc.

Nomenclature of the Isomeric Paraffins.—The simplest method for distinguishing the isomeric paraffins is to regard them as derivatives of some simpler paraffin, methane or ethane, in which one or more hydrogen atoms are replaced by "methyl," "ethyl," "propyl," etc., groups. A recently adopted method of nomenclature is to select the longest chain and regard it as the parent hydrocarbon, indicating by numbers the position of the side-chain radicals. Thus isopentane, $(CH_3)_2CH{\cdot}CH_2{\cdot}CH_3$, might be described as 2-methyl butane:



2-Methyl butane.



2:3-Dimethyl butane.

and dimethyl isopropyl methane as 2:3-dimethyl butane.

Iso-octane, $(CH_3)_3C{\cdot}CH_2{\cdot}CH(CH_3)_2$, is an important constituent of liquid fuels for internal-combustion engines, on account of its valuable "anti-knock" properties.

Questions on Chapter V.

1. Discuss the theory which accounts for the existence of homologues in the paraffin family.

2. Explain why the general formula of the paraffins is represented by C_nH_{2n+2}. What would n be if the vapour density of a paraffin were found to be 57?

3. How would you determine the purity of a sample of methane?

4. Calculate the proportion by volume of methane, hydrogen and nitrogen in a mixture which gave the following data on analysis:—10 c.c. of gas were made up to 90 c.c. with air and exploded. The volume then measured 73·75 c.c., and after absorption by potash, 69·75 c.c. Temperature and pressure were throughout constant.

5. What is meant by the *flashing-point?* How is it determined?

6. Write out the structural formulæ of the isomeric hexanes (C_6H_{14}), and name them.

7. Explain the meaning of the terms, normal, iso-, and neo-paraffins. How has the structure of ethane and neopentane been determined?

8. Give a method by which marsh-gas can be prepared. What are its properties? How would you obtain pure methane from a sample of coal-gas (methane, hydrogen, carbon monoxide, carbon dioxide, and benzene)?

9. How would you ascertain the composition and also the molecular weight of marsh-gas?

10. Discuss the industrial uses of the *paraffins*. What are the natural sources of these substances?

11. Describe the physical and chemical properties of the paraffins.

12. Explain the following terms: *additive compound, substitution product, saturated hydrocarbon*.

13. How has the structure of ethane, normal butane, and neopentane been ascertained?

14. Sketch formulæ for the first five terms of the series of normal paraffins, and show the number of isomers that may be obtained therefrom.

15. What is meant by the "law of substitution"? Give some examples showing its application in the determination of the valency of carbon.

16. What are the general properties of the paraffins? How is ethane prepared?

17. A mixture of hydrogen, marsh-gas, and nitrogen was mixed with air and exploded, and the residual gas submitted to the action of potash. From the following data calculate the percentage of the three constituents in the original mixture:—

Vol. of mixed gases	14·2 c.c.
Vol. of air added	83·4 ,,
Vol. after explosion	74·2 ,,
Vol. after absorption with potash	68·2 ,,

18. The molecular weight of a paraffin was determined by the boiling-point method from the following data: 0·1645 gram dissolved in 8·685 grams of benzene raised the boiling-point 0·135°. (Coefficient for benzene = 26·1.) Give the formula.

CHAPTER VI

HALOGEN DERIVATIVES OF THE PARAFFINS

The Halogen Derivatives of the Paraffins are formed, as we have seen, by substitution—that is, by the direct action of chlorine and bromine on the paraffins in presence of light. The iodine derivatives cannot be obtained in this way. The inertness of iodine is usually attributed to the liberation of hydriodic acid in the process, which, by its strong reducing action, immediately converts the iodine derivative into the original paraffin. This action is represented in the case of methane as follows—

$$CH_4 + I_2 = CH_3I + HI$$
$$CH_3I + HI = CH_4 + I_2.$$

According to the number of hydrogen atoms of the particular paraffin which are replaced by the halogen, the compounds are known as mono-, di-, tri-, etc., halogen derivatives of that paraffin.

Monohalogen Derivatives.—The most important of these substitution products are the monohalogen compounds. The following table contains the names, molecular formulæ, and boiling-points, of the first four members. The general formula is $C_nH_{2n+1}X$, in which X stands for the halogen atom.

TABLE IV.

MONOHALOGEN DERIVATIVES OF METHANE, ETC., $C_nH_{2n+1}X$.

		b.p.
Methyl chloride, or Chloromethane	CH_3Cl	−24°
Ethyl chloride, or Chlorethane	C_2H_5Cl	12·5°
Propyl chloride, or Chloropropane	C_3H_7Cl	44°
Isopropyl chloride, or Isochloropropane	C_3H_7Cl	36°
Methyl bromide, or Bromomethane	CH_3Br	4·5°
Ethyl bromide, or Bromethane	C_2H_5Br	38°
Propyl bromide, or Bromopropane	C_3H_7Br	71°
Isopropyl bromide, or Isobromopropane	C_3H_7Br	59°
Methyl iodide, or Iodomethane	CH_3I	43°
Ethyl iodide, or Iodethane	C_2H_5I	72°
Propyl iodide, or Iodopropane	C_3H_7I	102°
Isopropyl iodide, or Isoiodopropane	C_3H_7I	89°

The process of substitution is not often employed, because it is difficult to arrest the reaction after the first hydrogen atom has been replaced. The product of such a process is usually a mixture. Nevertheless attempts have been made in recent years to utilise this reaction for preparing such chlorine derivatives as methyl chloride, chloroform and carbon tetrachloride (p. 93) and also for conversion into methyl alcohol (see below). The pure substances are more conveniently obtained by acting upon the corresponding alcohols with the halogen acids. We may illustrate this reaction in the case of methyl alcohol or ethyl alcohol and hydrochloric acid—

$$\underset{\text{Methyl alcohol.}}{CH_4O} + HCl = \underset{\text{Methyl chloride.}}{CH_3Cl} + H_2O$$

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} + HCl = \underset{\text{Ethyl chloride.}}{C_2H_5Cl} + H_2O$$

In this reaction water is formed, but it is found that, by the action of water on the halogen compound, the original alcohol and the halogen acid are reproduced. Such reactions are known as *reversible*, and are usually indicated by writing the equation with arrows pointing two ways—

$$C_2H_6O + HCl \rightleftarrows C_2H_5Cl + H_2O.$$

It implies that the process is never completed in one direction, but that when a certain proportion of the products has been formed, a condition of equilibrium is reached. This proportion varies with the relative quantity of the reacting substances, the temperature, etc. We may suppose in the present instance that, for a given number of molecules of ethyl chloride and water which are formed from the alcohol and acid, a certain number of molecules of ethyl alcohol and hydrochloric acid are produced from the ethyl chloride and water. These reversible reactions play an important part in many organic processes, and are often met with when the reacting substances and their products are all present in solution. If, however, one of the products is removed, the condition of equilibrium is disturbed, and the reaction may be completed. In the above example, the presence of a dehydrating agent (zinc chloride) greatly accelerates the decomposition by removing water, which is no longer able to act on the ethyl chloride.

EXPT. 16. *Preparation of Ethyl Chloride.*—The apparatus is shown in Fig. 44. It consists of a stout flask, *a*, for generating hydrochloric acid gas. Strong sulphuric acid is dropped from a tap-funnel on to a mixture of strong hydrochloric acid and common salt (a layer about 1 inch deep covered with the acid).[1] The gas is passed through an empty vessel, *b*, and then into a flask, *c*, containing a mixture of ethyl alcohol and half its weight of coarsely powdered zinc chloride. The flask, which is heated on a water-bath, is provided with an upright condenser, from the top of which the vapour is conducted into a flask, *d*, containing water. The inlet-tube is cut off just above the surface

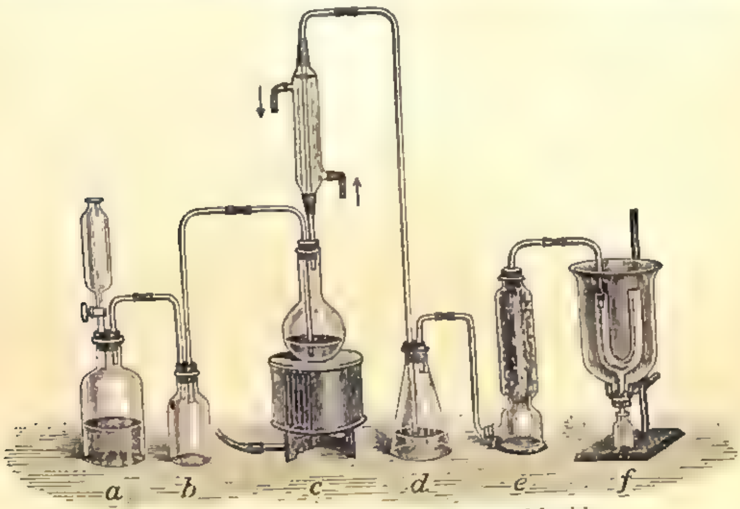


FIG. 44.—Preparation of Ethyl chloride.

of the water. Thence the vapour passes into the tower, *e*, filled with soda-lime, and finally into the U-tube, which is surrounded by ice. The condensed ethyl chloride drops from the bottom of the U-tube, and is collected in a small vessel, *f*, standing in ice. The condenser, which is attached to the flask, *c*, cools the alcohol vapour, and returns the liquid to the flask. The excess of hydrochloric acid gas which passes on is absorbed by the water in *d*, and what remains is removed by the soda-lime tower, *e*.

When the ethyl chloride begins to condense in *f*, the rubber-tube connection between the tower and the U-tube may be removed for a few moments, and the vapour of ethyl chloride ignited. It burns with a luminous smoky flame, which is fringed with green. This green mantle is characteristic of the flame of halogen compounds.

[1] A fairly rapid stream must be maintained on starting, or the alcohol will be sucked back into the vessel *b*.

Although hydrobromic and hydriodic acids are employed like hydrochloric acid for preparing the corresponding bromine and iodine compounds, the acids are troublesome to prepare, and bromine, or iodine, together with red phosphorus are often employed in their place.

EXPT. 17. *Preparation of Ethyl Bromide.*—Ten grams of red phosphorus and 70 c.c. of ethyl alcohol are placed in a distilling flask, attached to a condenser and receiver. The receiver is connected with a soda-lime tower. A tap-funnel containing 20 c.c. of bromine is fixed

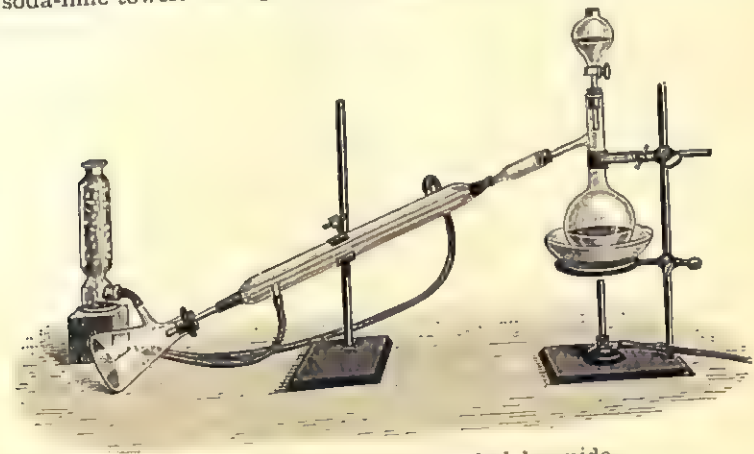


FIG. 45.—Preparation of Ethyl bromide.

through a cork in the neck of the distilling-flask. The apparatus is shown in Fig. 45. The flask is cooled in water and the bromine slowly added. The flask is then left for several hours, and the contents distilled from the water-bath. The soda-lime tower absorbs any fumes of hydrobromic acid which are evolved.

The distillate consists of ethyl bromide, which is purified by shaking it with a little sodium carbonate solution in a tap-funnel to remove both alcohol (which dissolves in the water) and hydrobromic acid (which combines with the sodium carbonate). The lower, and therefore heavier, insoluble layer is the ethyl bromide, which is withdrawn and separated from the water. It still contains a little water, which is removed by adding a few pieces of solid calcium chloride (dehydrating agent), and then re-distilling the liquid. *Ethyl iodide* is prepared as above, using iodine in place of bromine.

The action of the phosphorus and the halogen is usually ex-

plained by supposing that PBr_3 or PI_3 is formed, and that this reacts with the alcohol—

$$
P\begin{cases} Br & CH_3\,OH \\ Br + & CH_3\,OH \\ Br & CH_3\,OH \end{cases} = P\begin{cases} OH \\ OH \\ OH \end{cases} + 3CH_3Br.
$$

Phospnorus bromide. Methyl alcohol. Phosphorus acid. Methyl bromide.

It may be observed that phosphorus chloride gives methyl chloride together with methyl hydrogen phosphite—

$$PCl_3 + 3CH_4O = (CH_3O)P(OH)_2 + 2CH_3Cl + HCl.$$

Properties of Halogen Derivatives.—The physical properties of all the halogen derivatives may be gathered from a study of ethyl bromide, or of chloroform. They possess a sweet penetrating smell and are nearly all heavier than water, in which they are insoluble. They do not burn readily, and indeed some, like chloroform, are not inflammable. A few of them are used as anæsthetics, either for inhaling, like chloroform, or for producing local insensibility by freezing, like methyl and ethyl chloride (p. 79).

The importance of the monohalogen derivatives depends on the great variety of chemical changes which they undergo. We notice here a great difference between them and the paraffins. It is evidently due to the halogen atom, which is more easily removed than hydrogen, especially if the halogen is bromine or iodine.

Synthetic Processes in which Halogen Derivatives are used.—The following series of changes should be carefully studied and committed to memory. They represent the chief synthetic processes which will be hereafter studied.

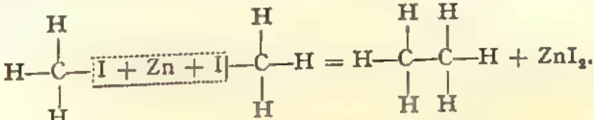
Methyl iodide is selected, because it is the simplest type of a monohalogen derivative; but the same kind of result is obtained with the ethyl, propyl, etc., compounds.

1. By the reducing action of the zinc-copper couple, the corresponding paraffin is formed (p. 69)—

$$
\begin{array}{c} H \\ | \\ H-C-\boxed{I + H}H \\ | \\ H \end{array} = \begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array} + HI.
$$

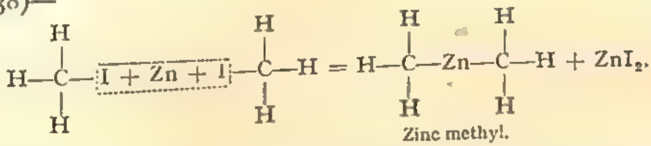
Methane.

2. Sodium or zinc gives the homologue, ethane (p. 72)—



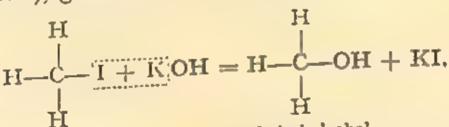
Ethane.

3. A similar reaction, but with excess of zinc, yields zinc methyl (p. 238)—



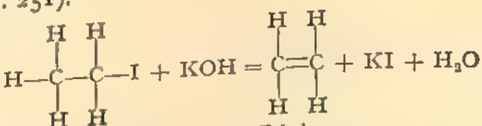
Zinc methyl.

4. Water, in presence of a basic oxide or hydroxide (KOH, Ag_2O, PbO, etc.), gives the alcohol (p. 103)—



Methyl alcohol.

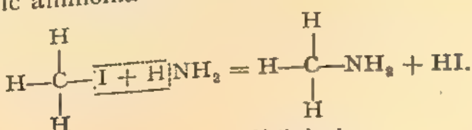
5. Alcoholic potash (a solution of caustic potash in alcohol) removes a molecule of hydriodic acid. A hydrocarbon is formed with 2 atoms less hydrogen than the corresponding paraffin. Thus, ethyl iodide gives ethylene, C_2H_4; propyl iodide forms propylene, C_3H_6, etc. (p. 251).



Ethylene.

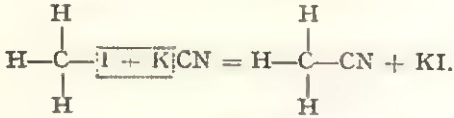
Methyl halides react differently from all the others, the radical *methylene*, CH_2, not having been isolated. Dimethyl ether, $(CH_3)_2O$ (p. 118), is formed instead.

6. Alcoholic ammonia forms methylamine (p. 205)—



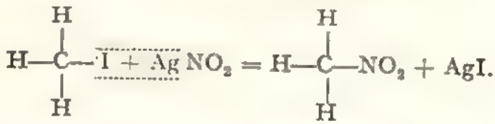
Methylamine.

7. Potassium cyanide gives methyl cyanide (p. 225)—



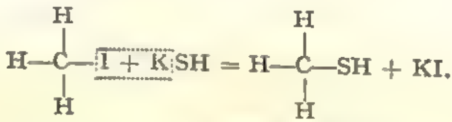
Methyl cyanide.

8. Silver nitrite forms nitromethane (p. 192)—



Nitromethane.

9. Potassium hydrosulphide yields methyl hydrosulphide, or methyl mercaptan (p. 196)—



Methyl mercaptan.

10. Magnesium combines with alkyl halides in the presence of pure dry ether to give an important addition compound (Grignard's reagent) (p. 242) CH_3MgI.

Radicals.—It will be noticed that in all these reactions the group $—CH_3$ remains intact, and preserves its individuality like a single univalent atom. Adopting an idea of Lavoisier, the group of atoms which, like methyl, plays the part of an element has been termed a *radical,* though it may have no existence apart from the compounds.

The relation of the radical, methyl, to the atom of hydrogen is well shown in the following parallel series of reactions :—

$$\mathbf{H}\boxed{Cl + K}OH = \mathbf{H}OH + KCl. \qquad \mathbf{CH_3}\boxed{Cl + K}OH = \mathbf{CH_3}OH + KCl.$$

$$\mathbf{H}\boxed{Cl + K}CN = \mathbf{H}CN + KCl. \qquad \mathbf{CH_3}\boxed{Cl + K}CN = \mathbf{CH_3}CN + KCl.$$

$$\boxed{\begin{matrix}\mathbf{H}Cl \\ \mathbf{H}Cl\end{matrix} = Zn} + \begin{matrix}\mathbf{H} \\ | \\ \mathbf{H}\end{matrix} + ZnCl_2. \qquad \boxed{\begin{matrix}\mathbf{CH_3}Cl \\ \mathbf{CH_3}Cl\end{matrix} + Zn} = \begin{matrix}\mathbf{CH_3} \\ | \\ \mathbf{CH_3}\end{matrix} + ZnCl_2.$$

The term radical originally implied a certain fixity of combination among the elements composing the radical ; but this view has

vanished. We do not now imagine that the 3 hydrogen atoms in the group CH_3 are more firmly attached to carbon than the fourth atom in methane.

Nomenclature of the Halogen Derivatives.—The mono-halogen compounds may therefore be regarded as combinations of the radical with the halogen. Methyl chloride, CH_3Cl, may be compared with hydrogen chloride, HCl, or with sodium chloride, NaCl, with this difference that these organic halides are not ionised. The generic term for the univalent radicals of the aliphatic series is **alkyl** (an abbreviated form of *alcohol* and *yl*, the termination of the name of the radicals, these groups being formerly known as alcohol radicals, p. 66). Methyl, ethyl, etc., are termed alkyl groups. But there is a second system in use for naming these compounds. The names may be derived from those of the related paraffins. In this case the name of the halogen precedes that of the paraffin. Chloromethane is synonymous with methyl chloride. This position of the halogen in the name always indicates a derivative of the hydrocarbon the name of which follows.

Propyl and Isopropyl Halides.—By reference to Table IV. it will be seen that the halogen compounds with 3 carbon atoms exist in two isomeric forms, which are readily distinguished by their properties, boiling-points, specific gravities, etc., and by the nature of their derivatives. The isomerism here is accounted for on the same principle as that of the two isomeric butanes (p. 74). The atom of the halogen, which we may denote by X, may be attached, like one of the methyl groups in butane, either to an end or middle carbon atom—

$$CH_3{\cdot}CH_2{\cdot}CH_2X. \qquad CH_3{\cdot}CHX{\cdot}CH_3.$$

The propyl and isopropyl halides are prepared from the respective alcohols (p. 95); isopropyl iodide is most easily obtained by the action of hydriodic acid on glycerol (p. 281)—

$$\underset{\text{Glycerol.}}{C_3H_8O_3} + 5HI = \underset{\substack{\text{Isopropyl}\\ \text{iodide.}}}{C_3H_7I} + 3H_2O + 2I_2.$$

Butyl Halides.—Each of the butyl halides exists in four isomeric forms; the structure of two of these may be derived from normal butane, and the remaining two from isobutane—

$$\underset{\text{Butane.}}{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3} \begin{array}{ll} \nearrow CH_2X{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3. & (1) \\ \searrow CH_3{\cdot}CHX{\cdot}CH_2{\cdot}CH_3. & (2) \end{array}$$

$$\underset{\text{Isobutane.}}{CH_3{\cdot}CH\begin{array}{l} \diagup CH_3 \\ \diagdown CH_3 \end{array}} \begin{array}{ll} \nearrow CH_2X{\cdot}CH\begin{array}{l} \diagup CH_3 \\ \diagdown CH_3 \end{array} & (3) \\ \searrow CH_3{\cdot}CX\begin{array}{l} \diagup CH_3 \\ \diagdown CH_3 \end{array} & (4) \end{array}$$

The position occupied by the halogen is of some importance, and is denoted in the following way :—When the halogen is attached to an end carbon atom, or is present in a group, $\cdot CH_2X$, the group is called a *primary* group. Where the halogen is attached to a carbon atom linked to not more than two others or, in other words, forms a group $\colon CHX$, it is termed a *secondary* group. Similarly, when the halogen is attached to a central carbon linked to three others, it forms a group $\vdots CX$, which is called a *tertiary* group. In the above example 1 and 3 contain primary, 2 a secondary, and 4 a tertiary group. The position of the halogen is denoted by the use of these terms in conjunction with the name of the paraffin. Both 1 and 3 are primary compounds; but the first is a derivative of normal butane, the second of isobutane. The names run as follows :—

$CH_2X{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	normal (primary) butyl halide.
$CH_3{\cdot}CHX{\cdot}CH_2{\cdot}CH_3$	(normal) secondary butyl halide.
$CH_2X{\cdot}CH\begin{array}{l} \diagup CH_3 \\ \diagdown CH_3 \end{array}$	primary isobutyl halide.
$CH_3{\cdot}CX\begin{array}{l} \diagup CH_3 \\ \diagdown CH_3 \end{array}$	tertiary (iso)butyl halide.

The names in brackets may be omitted, as their omission leads to no confusion.

Dihalogen Derivatives.—These compounds may be regarded as paraffins in which two atoms of hydrogen are replaced by two atoms of the halogen, or as combinations of a bivalent radical with the halogen. Thus, CH_2Cl_2 may be called dichloromethane, or it may be regarded as a compound of the type of calcium chloride, $Ca''Cl_2$, in which the bivalent group, CH_2'', plays the part of the calcium atom, and is united to chlorine. The names of the bivalent

or **alkylene** radicals are derived from the univalent radicals, with the additional suffix "-ene"—

CH_2'' methylene.
C_2H_4'' ethylene.
C_3H_6'' propylene, etc.

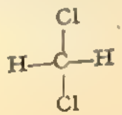
The compound CH_2Cl_2 is therefore called methylene chloride. These radicals are not purely hypothetical groups, like the univalent radicals; for, with the exception of the first, they represent compounds which exist in the free state. They will be described later (p. 246).

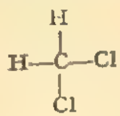
TABLE V.

DIHALOGEN DERIVATIVES, $C_nH_{2n}X_2$.

		B.p.
Methylene chloride, or Dichloromethane	CH_2Cl_2	41°
Ethylene chloride, or symm. Dichlorethane	$C_2H_4Cl_2$	84°
Ethylidene chloride, or unsymm. Dichlorethane	$C_2H_4Cl_2$	58°
Methylene bromide, etc.	CH_2Br_2	81°
Ethylene bromide, etc.	$C_2H_4Br_2$	131°
Ethylidene bromide, etc.	$C_2H_4Br_2$	110°
Methylene iodide, etc.	CH_2I_2	182°
Ethylene iodide, etc.	$C_2H_4I_2$	M.p. 81°
Ethylidene iodide, etc.	$C_2H_4I_2$	178°

It will be noticed that the plane structural formula for methylene chloride admits of two groupings of the atoms—





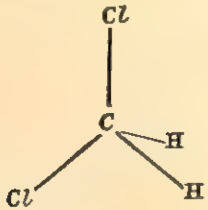


FIG. 46.

Yet only one methylene chloride, bromide, or iodide is known. The difficulty is met by supposing that the four bonds of the carbon

atom, are not in one plane, but have a space arrangement, represented in Fig. 46, which must be regarded as viewed in perspective.

Only one methylene compound is possible by this structural formula. There are, however, much more weighty reasons for adopting a space arrangement of the 4 carbon bonds, which will be considered later.

Ethylene and Ethylidene Compounds.—It will be noticed in Table V. (p. 87) that there are two isomeric compounds of the general formula $C_2H_4X_2$, each one of the pair being readily distinguished from the other by its boiling-point. One is formed by the action of the halogen on ethane, and in other ways (p. 126), the other by the union of ethylene with the halogen (p. 247). The existence of these isomers is at once apparent, if we suppose the two halogen atoms to be differently distributed between the carbon atoms—

$$\begin{array}{c} CH_2X \\ | \\ CH_2X \end{array} \qquad\qquad \begin{array}{c} CH_3 \\ | \\ CHX_2 \end{array}$$

The first is termed an *ethylene* compound, or symmetrical dihalogen derivative of ethane, the second an *ethylidene*, or unsymmetrical compound, ethylene denoting the bivalent radical $CH_2'{\cdot}CH_2'$, and ethylidene, the bivalent radical $CH_3{\cdot}CH''$. To which substance are we to assign the first, and to which the second formula?

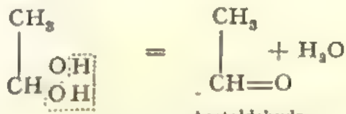
We must fall back upon a property of the halogen compounds which has already been mentioned, viz. that of exchanging the halogen atom for a hydroxyl (OH) group by the action of water in presence of a metallic oxide (p. 83). If we apply this reaction here, we should anticipate the formation of dihydroxy-compounds in both cases—

$$\begin{array}{l} CH_2\boxed{X \quad H}OH \\ | \\ CH_2\boxed{X \quad H}OH \end{array} \qquad\qquad \begin{array}{l} CH_3 \\ | \\ CH\begin{array}{l}\boxed{X \quad H}OH \\ \boxed{X \quad H}OH\end{array} \end{array}$$

I. II.

The one dihalogen compound does in fact give a dihydroxy-compound, known as glycol, $C_2H_6O_2$ (p. 275), the other yields acetaldehyde of the formula C_2H_4O. The formation of acetaldehyde is readily explained on the assumption that the compound

having formula II. loses the elements of a molecule of water. It is more probable that such a change occurs in the compound of formula II. where the two hydroxyl groups are joined to the same carbon atom, than in the other case, wherein they are united to different carbon atoms—



Acetaldehyde.

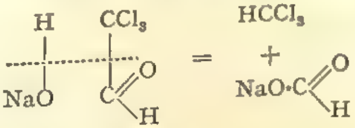
It is found that one of each pair of ethylene compounds having the lower boiling-point yields acetaldehyde, and this is therefore termed the unsymmetrical, or ethylidene compound.

Ethylene chloride, prepared from ethylene, is a commercial product and is used as an extractive solvent for fats, etc., and also for the manufacture of ethylene glycol (p. 275).

Trihalogen Derivatives.—Two members of this group are of great technical importance. Chloroform, or trichloromethane, and iodoform, or tri-iodomethane, are used in surgery and medicine on an extensive scale.

Chloroform, $CHCl_3$.—The word is derived from the old and obsolete name of the tervalent radical CH''', *formyl*. Chloroform was discovered by Liebig in 1831, and its anæsthetic action was first pointed out in 1848 by Simpson, who introduced it into surgery. It may be prepared in the pure state by distilling chloral with caustic soda, which yields chloroform and sodium formate.

The structural formulæ for chloral (trichloracetaldehyde) and formic acid must at present be accepted. They will be more fully discussed in subsequent chapters (pp. 147, 149).



Chloroform.

Sodium formate.

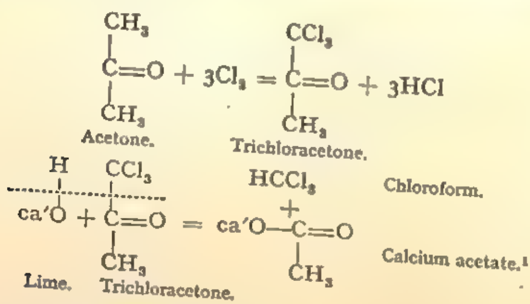
Caustic soda. Chloral.

Chloroform is usually manufactured by boiling ethyl alcohol, or acetone, C_3H_6O, with bleaching-powder and water. The reaction in either case is complex, and probably represents a series of changes. The bleaching-powder may be considered as furnishing

both chlorine and lime. The alcohol is converted by the chlorine into chloral, which is then decomposed by the lime, as it is with an alkali, into chloroform and calcium formate—

$$\underset{}{C_2H_6O} + 4Cl_2 = \underset{\text{Chloral.}}{C_2Cl_3HO} + 5HCl.$$

The acetone forms trichloracetone, which splits up when heated with lime into chloroform and calcium acetate. The structure of acetone and acetic acid must be assumed in order to understand the course of the reaction.



EXPT. 18. *Preparation of Chloroform.*—A round 2-litre flask is fitted with a cork, through which a bent tube passes, connecting the flask with a long condenser and receiver. The flask is placed upon a large sand-bath. The bleaching-powder (200 grams) is ground into a paste with water (800 c.c.). Fifty c.c. of acetone are now added, and the contents heated cautiously until the reaction begins. The flame is removed for a time until the reaction has moderated. The liquid is then boiled until no more heavy drops distil with the water. The distillate is purified by exactly the same process as that described in the preparation of ethyl bromide (p. 81).

Chloroform is a heavy, colourless liquid, b.p. 61°–62°, m.p. −63·2°, and sp. gr. 1·525. It is non-inflammable. When pure, dry chloroform is exposed to sunlight and air, especially when calcium chloride is present, free chlorine and carbonyl chloride are rapidly formed—

$$2CHCl_3 + 3O = H_2O + 2COCl_2 + Cl_2.$$

[1] By taking calcium as univalent, or as representing a half atom, the equation is simplified. Otherwise the number of molecules on both sides of the equation would require to be doubled.

The addition of about 1 per cent. of alcohol arrests this change but even then it is desirable to keep the liquid in the dark, and the bottle filled to the neck.

The presence of the products of the above decomposition is readily ascertained by adding silver nitrate solution, which has no action on pure chloroform, but forms silver chloride when either carbonyl chloride or chlorine is present. For anæsthetic purposes the presence of either impurity is extremely dangerous. Chloroform should leave no residue on evaporation.

The presence of chloroform is detected by its smell. A more

FIG. 47.—Test for Chloroform.

delicate test is known as the *phenyl carbamine*, or *isocyanide reaction*. This test depends upon the action of chloroform upon aniline in the presence of caustic potash, which gives phenyl carbamine, a compound with an intolerable smell—

$$CHCl_3 + \underset{\text{Aniline.}}{C_6H_5NH_2} + 3KOH = \underset{\text{Phenyl carbamine}}{C_6H_5NC} + 3KCl + 3H_2O.$$

EXPT. 19.—The following reaction should be performed in a fume cupboard. Bring into a test-tube two drops of chloroform, one drop of aniline, and 1 c.c. of alcoholic potash (caustic potash dissolved in alcohol), and warm. Notice the smell of phenyl carbamine.

Chloroform may also be detected by boiling the substance under examination (which must not contain free acid), with water, and passing the vapour through a heated tube. The chloroform breaks

up, on heating, into hydrochloric acid and chlorine, which are indicated by their action on a piece of blue litmus paper held at the mouth of the tube.

EXPT. 20.—A flask furnished with a bent delivery-tube may be used (Fig. 47). Water containing a few drops of chloroform is introduced into the flask and gently boiled, the delivery-tube being heated by a second burner. A piece of blue litmus held at the end will be rapidly reddened and then bleached, or potassium iodide and starch paper will be turned blue.

Iodoform, CHI_3, is prepared from alcohol or acetone by the action of iodine and an alkali or by using a mixture of sodium hypochlorite and sodium iodide. The process is probably analogous to the formation of chloroform.

EXPT. 21. *Preparation of Iodoform.*—Two parts of crystallised sodium carbonate are dissolved in 10 parts of water; one part of ethyl alcohol is poured into the solution, and then one part of iodine gradually added. The liquid is kept at 60°–80°, when iodoform gradually separates.

Iodoform is decomposed, on boiling with caustic alkalis, into potassium formate—

$$\mathrm{HC}\begin{cases}\mathrm{I} \\ \mathrm{I} \\ \mathrm{I}\end{cases} + \begin{matrix}\mathrm{KOH}\\ \mathrm{KOH}\\ \mathrm{KOH}\end{matrix} \rightarrow \mathrm{HC}\begin{cases}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{cases} \rightarrow \mathrm{HC}\begin{cases}\mathrm{OH}\\ \mathrm{O}\end{cases} + \mathrm{H_2O}.$$

Iodoform. Ortho-formic acid (not known). Formic acid.

Hence, in preparing iodoform with caustic alkali in place of the carbonate, it is desirable not to boil the solution.

Iodoform is also prepared commercially by the electrolysis of a solution of potassium iodide in presence of alcohol or acetone.

EXPT. 22.—*Preparation of Iodoform by Electrolysis.*—Twenty grams of sodium carbonate (anhydrous) and 20 grams of potassium iodide are dissolved in 200 c.c. of water and 50 c.c. of absolute alcohol added, and poured into a beaker. The anode consists of a sheet of platinum foil 8 × 10 cms., and the cathode of platinum wire wound into a spiral of 1 cm. diameter. The solution is warmed to 60°–70° and a current of 3 amps. per sq. decimetre passed through the solution, whilst carbon dioxide is allowed to bubble into the liquid. In about 30 minutes a quantity of iodoform will have separated.

On electrolysis, iodine is liberated from the potassium iodide,

which, in presence of the alkaline carbonate, acts upon the alcohol or acetone in the ordinary way and hydrogen is evolved :—

$$2KI + H_2O + CO_2 = K_2CO_3 + H_2 + I_2.$$

Iodoform crystallises in lemon-yellow hexagonal plates or star-shaped crystals, which have a characteristic appearance under the microscope. It melts at 119°, and sublimes. It is used in medicine and surgery as a strong antiseptic and disinfectant; but, on account of its peculiar and unpleasant smell, other organic iodine compounds have been prepared as substitutes (p. 566).

Carbon Tetrachloride, CCl_4, is now manufactured on a commercial scale, and is used as a solvent. It is obtained by the action of chlorine on carbon bisulphide in the presence of a little metallic iron, which assists the reaction, as a " chlorine carrier " :—

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2,$$
$$CS_2 + 2S_2Cl_2 = CCl_4 + 6S.$$

Carbon tetrachloride is a colourless liquid, with a sweet smell like chloroform. It boils at 76°–77°. It does not decompose in sunlight like chloroform. As it is non-inflammable it is used in dry cleaning and for other commercial purposes.

Tetrachlorethane or Acetylene tetrachloride, $C_2H_2Cl_4$, is prepared by the interaction of acetylene (p. 263) and chlorine in presence of antimony chloride. By the action of lime it is transformed into trichlorethylene, C_2HCl_3, and with metals into dichlorethylene, $C_2H_2Cl_2$, and the two latter by further chlorination into C_2HCl_5, C_2Cl_4 and C_2Cl_6. All these compounds are utilised either as solvents or in organic synthesis.

Questions on Chapter VI

1. Calculate the theoretical weight of bromine and hydrochloric acid, respectively, required to convert 10 grams of ethyl alcohol into ethyl bromide and ethyl chloride; also the theoretical weights of the two products.

2. Give the formulæ for any two primary, any two secondary, and any two tertiary, hexyl iodides.

3. What paraffins could be obtained from ethyl alcohol? Explain the steps.

4. Formulate the action of metallic sodium, ammonia, potassium cyanide, dilute caustic potash, and strong alcoholic potash on ethyl bromide.

5. Explain the solvent action of boiling caustic potash on iodoform. By analogy, what would be the action of the same alkali on chloroform and carbon tetrachloride?

6. How would you explain the isomerism and determine the structure of ethylene and ethylidene chlorides?

7. What is the meaning of the term *compound radical?* Give examples of a mono-, di-, and tervalent radical.

8. Explain the formation of chloroform from alcohol and acetone. Give the tests for chloroform.

9. How would you determine the purity of a specimen of chloroform? What impurities is it likely to contain?

10. Name the *alkyl* groups in the following formulæ: C_2H_5I; $CH_3{\cdot}CHCl{\cdot}CH_3$; $(CH_3)_2CH{\cdot}CH_2Br$.

11. Describe and explain the formation of iodoform. What are its chief properties?

12. How is chloroform prepared? What reactions prove it to be a derivative of methane? How can the presence of chlorine be shown?

13. Suppose a small quantity of chloroform which contains some water has been exposed to sunlight in a large colourless glass bottle, would the chloroform be pure, and, if not, how would you test for the impurities?

14. How is ethyl bromide prepared? How does ethyl bromide react with (1) caustic potash, (2) ammonia, (3) sodium?

15. Describe a method for the preparation of methyl iodide. How would you determine its vapour density?

16. Two isomeric compounds having the composition $C_2H_4Cl_2$ are known; how are these compounds obtained, and how has their constitution been determined?

17. What is iodoform? Describe by equations how it is prepared. What is produced on boiling it with a solution of caustic potash in alcohol?

18. What is the origin of the name "chloroform"?

CHAPTER VII

THE ALCOHOLS

THE alcohols may be looked upon as hydroxyl derivatives of the paraffins. The general formula is $C_nH_{2n+1}OH$ which represents a paraffin with an additional atom of oxygen. A list of the more important alcohols, with their boiling-points and specific gravities, is given in Table VI.

TABLE VI.

THE ALCOHOLS, $C_nH_{2n+2}O$.

		B.p.	Sp. gr.
Methyl alcohol (Methanol)	$CH_3(OH)$	66°	·812
Ethyl alcohol (Ethanol) .	$C_2H_5(OH)$	78°	·806
Propyl alcohols (Propanols)	$C_3H_7(OH)$		
Primary	$CH_3{\cdot}CH_2{\cdot}CH_2(OH)$	97°	·804
Secondary (Isopropyl) .	$CH_3{\cdot}CH(OH){\cdot}CH_3$	85°	·789
Butyl alcohols (Butanols)	$C_4H_9(OH)$		
Normal primary . .	$C_2H_5{\cdot}CH_2{\cdot}CH_2(OH)$	117°	·810
Normal secondary . .	$C_2H_5{\cdot}CH(OH){\cdot}CH_3$	100°	·819
Primary isobutyl . .	$(CH_3)_2CH{\cdot}CH_2(OH)$	107°	·806
Tertiary	$(CH_3)_2C(OH){\cdot}CH_3$	83°	·786
Amyl alcohols (Pentanols)	$C_5H_{11}(OH)$		
Normal primary . .	$C_2H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2(OH)$	138°	·815
Isobutyl carbinol . .	$(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2(OH)$	131°	·810
Secondary butyl carbinol	$CH_3{\cdot}CH{\cdot}(C_2H_5){\cdot}CH_2OH$	128°	—
Tertiary butyl carbinol	$(CH_3)_3C{\cdot}CH_2(OH)$	112°	—
Methyl propyl carbinol	$C_2H_5{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$	119°	—
Methyl isopropyl carbinol	$(CH_3)_2CH{\cdot}CH(OH){\cdot}CH_3$	114°	—
Diethyl carbinol . .	$C_2H_5{\cdot}CH(OH){\cdot}C_2H_5$	117°	—
Dimethylethyl carbinol	$(CH_3)_2C(OH){\cdot}C_2H_5$	102°	—

General Properties of Alcohols.—The alcohols are colourless and neutral substances, having neither an acid nor alkaline reaction. The lower members, viz. those with few carbon atoms, are liquids;

the higher members are solids. The lower members have a burning taste and distinctive smell, and are more or less soluble in water; but taste, smell, and solubility in water rapidly diminish with increasing molecular weight. Methyl, ethyl, and propyl alcohol are miscible with water; butyl alcohol dissolves in 12 parts; amyl alcohol, from fusel oil, requires 39 parts of water. The proportion of oxygen appears to determine the solubility in water, and as it decreases with increasing molecular weight, the general physical characters of the paraffin gradually predominate. Cetyl alcohol, $C_{16}H_{34}O$, derived from spermaceti, is a solid, quite insoluble in water, and greasy to the touch like paraffin-wax.

Constitution of the Alcohols.—In spite of physical differences, the *chemical* behaviour of the alcohols persists throughout the series. In certain reactions, the alcohols resemble water; in others, again, they show a closer similarity with caustic soda. Like water, they are decomposed by sodium, and hydrogen is liberated; but, whichever alcohol is taken, only one atom of hydrogen is liberated and replaced by sodium.

EXPT. 23.—Throw a small piece of sodium into methyl or ethyl alcohol. There is a vigorous effervescence, but the heat given out is never sufficient to ignite the gas, as it may do when water is decomposed. When the sodium has dissolved, evaporate the solution on the water-bath to dryness. A white solid remains, which is very hygroscopic and is decomposed by water. The solid has the formula CH_3ONa, or C_2H_5ONa, according to the alcohol taken. The product is a definite compound, known as sodium methylate (methoxide), or sodium ethylate (ethoxide), or generally as *sodium alcoholate*.

We have already seen (p. 82) that an alcohol, like water, decomposes the chloride, bromide, and iodide of phosphorus.

EXPT. 24.—Add a small quantity of phosphorus pentachloride to a few c.c. of methyl or ethyl alcohol. Notice the vigorous action and the disengagement of hydrochloric acid fumes.

The relation between an alcohol and water may be illustrated by the following equations, in which methyl alcohol is taken as the typical alcohol :—

Water.	*Methyl Alcohol.*
$2H_2O+2Na=2HONa+H_2$.	$2CH_4O+2Na=2CH_3ONa+H_2$.
$H_2O+PCl_5=HCl+HCl+POCl_3$.	$CH_4O+PCl_5=CH_3Cl+HCl+POCl_3$.
$3H_2O+PBr_3=3HBr+H_3PO_3$.	$3CH_4O+PBr_3=3CH_3Br+H_3PO_3$.

In these reactions the radical *methyl* plays the part of hydrogen (see p. 84). Some of the alcohols also enter into the composition of certain crystalline inorganic salts, in which relation they offer an analogy with *water of crystallisation*. Examples of this character are the compounds of calcium chloride with methyl alcohol and ethyl alcohol—

$$CaCl_2 + 4CH_4O, \text{ and } CaCl_2 + 4C_2H_6O.$$

The correspondence subsisting between the alcohols and the caustic alkalis is best observed in their behaviour with the acids.

Taking methyl alcohol as representative of the alcohols, the following equations will explain the reactions which occur :—

Caustic Soda.	*Methyl Alcohol.*
$NaOH + HCl = NaCl + H_2O.$	$CH_4O + HCl = \underset{\text{Methyl chloride.}}{CH_3Cl} + H_2O.$
$NaOH + HNO_3 = NaNO_3 + H_2O.$	$CH_4O + HNO_3 = \underset{\text{Methyl nitrate.}}{CH_3{\cdot}NO_3} + H_2O.$
$NaOH + H_2SO_4 = NaHSO_4 + H_2O.$	$CH_4O + H_2SO_4 = \underset{\text{Methyl hydrogen sulphate.}}{CH_3{\cdot}H{\cdot}SO_4} + H_2O.$

Here the radical, methyl, plays the part of sodium, but the products are not salts, and as alcohols are not ionised the reactions are much slower than with bases.

We may then build up the graphic formula for methyl alcohol on the basis of the formula for water, or caustic soda—

$$H{-}O{-}H \qquad Na{-}O{-}H \qquad \begin{array}{c} \phantom{H{-}}H \\ \phantom{H{-}}| \\ H{-}C{-}O{-}H. \\ \phantom{H{-}}| \\ \phantom{H{-}}H \end{array}$$

The other alcohols will be similarly constituted. Ethyl alcohol may be written, $C_2H_5{\cdot}OH$; propyl alcohol, $C_3H_7{\cdot}OH$, etc.; the radicals methyl, ethyl, propyl, etc., playing the part of hydrogen in water, or sodium in caustic soda. As caustic soda is also termed sodium hydroxide, so the alcohol is sometimes denoted by the name of the hydroxide of the radical. *Methyl hydroxide* is synonymous with methyl alcohol. It was in consequence of the radicals being first recognised as constituents of the alcohols that they were formerly known as the *alcohol radicals*, a term which is now replaced by the word **alkyl**.

The above graphic formula for the alcohols explains many things which would not be apparent from the simple molecular formula. Thus, only one atom of hydrogen is replaceable by sodium. This atom of hydrogen possesses a different function from the rest, and is evidently the one which is linked to oxygen.

Then, again, by the action of chloride or bromide of phosphorus, the oxygen atom and one atom of hydrogen are removed together, and replaced by an atom of the halogen. The change is readily explained by the above formula, which contains an atom of oxygen and hydrogen linked together, forming the hydroxyl group —OH. This group, which often forms part of an organic molecule, retains, in the majority of cases, its chemical properties unchanged. Its presence may generally be determined by the action of sodium or phosphorus chloride, which produces, as a rule, the same chemical change as in the alcohols.

There are other methods for detecting the presence of the hydroxyl group, which need not be discussed at present.

Other Chemical Properties of the Alcohols.—In addition to the reactions mentioned above, the alcohols undergo other chemical changes of importance. Strong sulphuric acid reacts with the alcohols to form the alkyl hydrogen sulphates. If these compounds are heated, sulphuric acid is separated, and hydrocarbons of the general formula C_nH_{2n} are formed. The latter are termed **olefines**, and are treated more fully in Chap. XVII. (p. 246). Ethyl alcohol gives ethyl hydrogen sulphate and ethylene—

$$\underset{\text{Ethyl alcohol.}}{C_2H_5OH} + H_2SO_4 = \underset{\substack{\text{Ethyl hydrogen}\\\text{sulphate.}}}{C_2H_5{\cdot}H{\cdot}SO_4} + H_2O.$$

$$C_2H_5{\cdot}H{\cdot}SO_4 = \underset{\text{Ethylene.}}{C_2H_4} + H_2SO_4.$$

The olefines are directly obtained by heating the alcohol to a moderately high temperature with a large excess of concentrated sulphuric acid. The process is most simply explained by supposing that the elements of a molecule of water are removed from the alcohol by the dehydrating action of the sulphuric acid—

$$C_2H_6O—H_2O = C_2H_4,\ \text{Ethylene},$$
$$C_3H_8O—H_2O = C_3H_6,\ \text{Propylene, etc.}$$

Methyl alcohol does not form methylene, CH_2, which is unknown

(see p. 83); but yields dimethyl sulphate, $(CH_3)_2SO_4$, by this reaction (p. 189).

EXPT. 25. Put a little sand or anhydrous aluminium sulphate into a round flask of about 1 litre capacity, pour in 60 c.c. of strong sulphuric acid, and add gradually 20 c.c. of ethyl alcohol. Fit a long, wide, upright tube by a cork to the neck of the flask, and heat the flask and its contents on wire-gauze over a moderate flame (see Fig. 48, p. 105). After a time the mixture darkens and effervesces. Ethylene gas is evolved, and may be ignited at the end of the upright tube, where it burns with a bright luminous flame.

It should be noticed that the compounds prepared in this way are identical with those obtained by the action of alcoholic potash on the alkyl halides (p. 251).

If, instead of an excess of strong sulphuric acid, an excess of the alcohol is present, the reaction which occurs is of quite a different character, and the products formed are termed **ethers.** They will be considered in the following chapter. Thus, the action of sulphuric acid upon an alcohol is of a threefold character. At the ordinary temperature the two react to produce the alkyl sulphate; at high temperatures, with excess of sulphuric acid, hydrocarbons are produced; with excess of alcohol, ethers are formed. This is one of many examples which might be given of an organic reaction wherein a change in the conditions produces a marked alteration in the nature of the products.

The alcohols readily undergo oxidation.

EXPT. 26. Warm a solution of potassium dichromate, acidified with dilute sulphuric acid, with a few drops of alcohol. The solution soon becomes green from the reduction of the dichromate to chromic sulphate, and, at the same time, a peculiarly penetrating smell is evolved. The smell is that of the substance known as *acetaldehyde*, and is the product of the oxidation of ethyl alcohol.

It is found that the different alcohols do not behave quite alike on oxidation. Some, like ethyl alcohol, form substances known as **aldehydes,** others form a class of compounds known as **ketones.** The difference in the behaviour of the alcohols on oxidation separates them into three well-defined groups, the *primary*, *secondary*, and *tertiary* alcohols.

Primary, Secondary, and Tertiary Alcohols.—These names are used in the same sense as that applied to the alkyl halides (p. 86). We have only to substitute a hydroxyl group for the halogen atom in the alkyl halides.

A **primary** alcohol has the hydroxyl group linked to an end carbon atom of the series, and contains the group $\cdot CH_2(OH)$.

A **secondary** alcohol has the hydroxyl group attached to a middle carbon atom of a straight chain, and contains the group $:CH(OH)$.

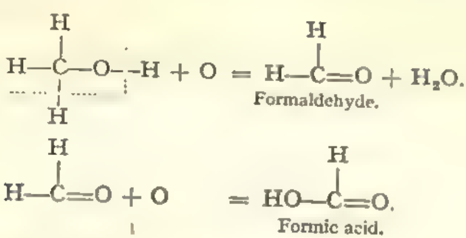
A **tertiary** alcohol contains the group $\vdots C(OH)$, *i.e.* the carbon atom attached to the hydroxyl group is linked to three carbon atoms.

$\cdot CH_2(OH)$, primary alcohol group.
$:CH(OH)$, secondary alcohol group.
$\vdots C(OH)$, tertiary alcohol group.

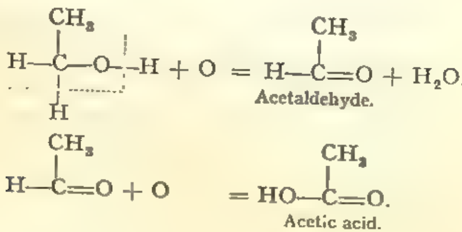
Examples of all three classes will be found in Table VI. (p. 95).

The primary alcohols on oxidation first lose 2 atoms of hydrogen and form *aldehydes ;* but the latter can be further oxidised, and, by taking up an additional atom of oxygen, are converted into *acids.*

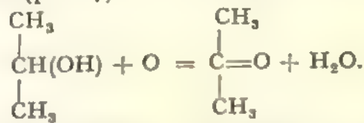
Thus, methyl alcohol first forms formaldehyde, and secondly formic acid (p. 126)—



Ethyl alcohol yields, by the same process, first acetaldehyde, and then acetic acid—

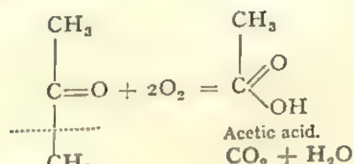


The secondary alcohols also lose two atoms of hydrogen in the first stage of oxidation. The compounds which are formed are termed *ketones*. Secondary or iso-propyl alcohol yields dimethyl ketone, or acetone (p. 127)—



Secondary, or iso-propyl alcohol. Dimethyl ketone.

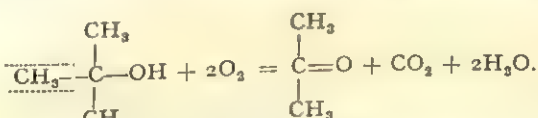
Further oxidation breaks up the ketone molecule into smaller fragments, consisting of acids belonging to the formic acid family, but containing fewer carbon atoms than the ketone. Dimethyl ketone yields, on oxidation, acetic acid, carbon dioxide, and water—



Acetic acid.

Dimethyl ketone. Carbon dioxide. Water.

The tertiary alcohols decompose on oxidation, forming ketones, or acids with fewer carbon atoms than the original alcohol. Tertiary butyl alcohol gives dimethyl ketone, carbon dioxide, and water—



Tertiary butyl alcohol. Dimethyl ketone.

Nomenclature of the Alcohols.—The division into primary, secondary, and tertiary alcohols, is not sufficient to describe a member belonging to a numerous family of isomers like that of the amyl or hexyl alcohols, which contain more than one representative of each of these groups. If they possess an unbranched chain, they may be regarded as derivatives of a normal paraffin, and the alcohol is termed a **normal alcohol**; in the same way an alcohol with a branched chain is termed an **iso-alcohol,** *i.e.* a derivative of an iso-paraffin. Examples of this kind will be noticed in Table VI. under the butyl alcohols. An alternative method for naming the alcohols which has been more recently introduced is to add the

termination "ol" to that of the related paraffin, *e.g.* methyl alcohol becomes *methanol*, ethyl alcohol *ethanol*, and so forth. Another system, which is also in use, was proposed by Kolbe. The carbon group which contains the hydroxyl group, whether primary, secondary, or tertiary, is termed the **carbinol** group. The radicals attached to this group are then named in conjunction with the word carbinol. To take a simple example, secondary propyl alcohol, may also be called *dimethyl carbinol;* tertiary butyl alcohol may be termed *trimethyl carbinol.* The application of this system is well illustrated in the case of the amyl alcohols (see Table VI.).[1]

Sources of the Alcohols.—The alcohols are found in nature as a constituent part of many vegetable and animal products of very varied character, such as certain oils, fats, and waxes; but the chief source, especially of the lower members, is **fermentation.** Ethyl, propyl, butyl, and amyl alcohol are all obtained by this process. Butyl alcohol together with acetone (p. 143) is obtained from starch by the action of a special ferment. Methyl alcohol is obtained by the distillation of wood and from water-gas (p. 103).

The synthetic methods for the production of the alcohols are very numerous. It has already been stated that aldehydes and ketones are formed by the oxidation of the alcohols. By the reverse process of reduction, aldehydes and ketones may be converted into the corresponding alcohols. Acetone, which is obtained from the products of distillation of wood, may be reduced, by sodium amalgam and water, to secondary propyl alcohol—

$$\underset{\text{Acetone.}}{CH_3{\cdot}CO{\cdot}CH_3} + H_2 = \underset{\text{Secondary propyl alcohol.}}{CH_3{\cdot}CH(OH){\cdot}CH_3}.$$

On p. 97, the action of the various acids upon the alcohols is explained. The products of the interaction are called **esters.** These reactions are all *reversible*, and consequently, methyl chloride, nitrate, and sulphate may be partially converted by water alone

[1] A more modern method of nomenclature is to take the longest chain which contains the alcohol group and name it from the corresponding paraffin with the termination -ol. The positions of the attached radicals are indicated by numbering the carbons, 1, 2, 3, etc., counting from the end nearest the hydroxyl group. Secondary butyl carbinol would be termed 2-methyl butan 1-ol, and diethyl carbinol would be called pentan 3-ol.

into the alcohol and free acid. The presence of caustic alkali, by forming the stable alkali salt with the free acid, usually accelerates this reaction—

$$CH_3Cl + HOH = CH_3(OH) + HCl.$$
$$CH_3{\cdot}NO_3 + HOH = CH_3(OH) + HNO_3.$$
$$CH_3{\cdot}H{\cdot}SO_4 + HOH = CH_3(OH) + H_2SO_4.$$

This reaction makes it possible to obtain an alcohol from a paraffin by chlorinating the latter and treating the product with alkali. The method is, however, not employed in practice, except in the case of the pentanes which are utilised in this way for making "pentasol" used in the lacquer industry:

$$C_5H_{12} \longrightarrow C_5H_{11}Cl \longrightarrow C_5H_{11}OH.$$

The conditions under which the different kinds of alkyl esters decompose most readily vary considerably, and must be studied individually.

The more complex methods for preparing alcohols will be discussed in later chapters (pp. 241, 243).

We will now consider in greater detail the production of a few of the more important alcohols.

Methyl Alcohol (Methanol), $CH_3{\cdot}OH$.—The name methyl is derived from μέθυ wine, and ὕλη wood. It is known commercially as *wood-spirit* or *wood-naphtha*. It was first prepared by Boyle in 1661 by the distillation of wood, and this is the process by which until recently most of the methyl alcohol was manufactured. When wood is subjected to destructive distillation, it yields inflammable gases, a strongly acid aqueous distillate, and a quantity of tar. The residue is wood charcoal. The operation is carried out in large iron retorts. The aqueous distillate contains the methyl alcohol mixed with acetic acid and acetone and a little methyl acetate, and is known as *pyroligneous acid* (see p. 160). The tar, which consists of paraffins, phenols (p. 455), and other organic substances, separates from the aqueous portion on standing, and the latter is then withdrawn. It is neutralised with lime, whereby the acetic acid is converted into the lime salt, and distilled. The volatile methyl alcohol and acetone, together with water, pass into the receiver. The crude wood-spirit is purified by fractional distillation over quicklime, which removes the greater part of the acetone (b.p. 56°) and water.

Methyl alcohol is also produced by the destructive distillation

of the by-products of the beet-root sugar industry (p. 305). The molasses are fermented and the ethyl alcohol removed by distillation. The residue is then dried and distilled like wood.

Commercial methyl alcohol prepared by the above methods always contains acetone, which may be reduced in amount by fractional distillation to 1 or 2 per cent.; but the quantity is frequently greater. There are various special methods for removing the last traces of acetone. Thus by chlorination of the hot liquid and fractional distillation the acetone remains as high boiling trichloracetone and the alcohol distils unchanged. The presence of acetone is readily shown by the iodoform reaction, which is described under ethyl alcohol (p. 113). To obtain methyl alcohol chemically pure, it is converted into the solid crystalline compound with calcium chloride (p. 97).

EXPT. 27.—A mixture of 75 grams of methyl alcohol and 50 grams of anhydrous calcium chloride is heated on the water-bath with inverted condenser until solution is obtained. On cooling, the compound $CaCl_2 + 4CH_3OH$ crystallises. When the calcium chloride compound is heated, pure methyl alcohol is driven off and is condensed and collected.

Synthetic methyl alcohol is now manufactured on a large scale by passing purified water gas ($CO + H_2$) mixed with more hydrogen at about 200 atmospheres pressure and at 400° over a catalyst consisting of a metallic oxide, zinc oxide or chromate or mixtures of metallic oxides.

$$CO + 2H_2 = CH_3OH.$$

Methyl alcohol boils at 66°. It is inflammable, and burns with a blue flame. It is used in the manufacture of certain coal-tar colouring matters, and for dissolving shellac and resins in the preparation of varnishes. It is mixed with ethyl alcohol in methylated spirit (p. 111), and is used for making formaldehyde.

Fermentation.—When yeast (saccharomyces) is added to a solution of grape- or cane-sugar, the liquid shortly begins to froth and has the appearance of boiling, although there is a scarcely perceptible rise of temperature. The process is called fermentation, from the Latin *fervere*, to boil. A fundamental change occurs in the sugar, whereby it is broken up into **ethyl alcohol**[1] and carbon dioxide.

[1] The word *ethyl* is derived from *αἰθήρ*, ether; *ὕλη*, substance, as ordinary ether contains the radical of ethyl alcohol (p. 121).

Expt. 28.—Dissolve 10 grams of grape-sugar in 200 c.c. of water; pour the solution into a large flask (2 litres), and add about an ounce of brewers' yeast. Fit the flask with a cork and bent delivery tube, dipping into lime-water. Warm the solution to about 25°, and leave the flask in a warm place. After a short time bubbles of gas appear, and a considerable deposit of calcium carbonate will form in the lime-water. After twenty-four hours the presence of alcohol in the flask may be readily ascertained by pouring out a small portion of the liquid into a flask furnished with an upright tube as shown in Fig. 48. On gently boiling the contents, the vapour of alcohol, which is more volatile than water, is the first to pass out of the open end of the upright tube, and may be ignited. Another portion of the contents of the flask may be distilled and the first few c.c. collected. Potassium carbonate (solid) is added to the distillate, and the supernatant liquid, which is the alcohol, separated. The liquid is then distilled over quicklime, and is found to boil at 78°.

Fig. 48.

This decomposition was first studied quantitatively by Lavoisier. It may be expressed, in the case of grape-sugar, by the following equation—

$$\underset{\text{Grape-sugar.}}{C_6H_{12}O_6} = \underset{\text{Ethyl alcohol.}}{2C_2H_6O} + \underset{\text{Carbon dioxide.}}{2CO_2}.$$

But the reaction is not so simple as the equation represents; for, in addition to ethyl alcohol, there appear propyl and isobutyl and the two amyl alcohols, viz. isobutyl carbinol and secondary butyl-carbinol, which together constitute *fusel oil.* Moreover, there is present about 0·6 per cent. of succinic acid and 2·5 per cent. of glycerol (see p. 279). The process of fermentation is one of great antiquity. It was well known that yeast, or the white scum which forms in the fermenting liquid, is capable of setting up fermentation in fresh quantities of saccharine solution. The yeast was first examined in 1680 by Leeuwenhoek, under the microscope, shortly after that instrument had been invented,

and was observed by him to consist of numerous small spherical granules; but it was not until 1836 that de la Tour in France and Schwann in Germany, independently, discovered the living nature of yeast cells. These cells, which are sometimes called the yeast plant, are now recognised as a low form of vegetable life. The cells are spherical, having, under a high power, the appearance represented in Fig. 48. The cell has a thin outer envelope of cellulose, and its contents consist of protoplasm. Reproduction takes place by budding, and the bud, having attained a certain size, detaches itself from the parent cell. The stages in the process are represented in Fig. 49. If the liquid is undisturbed, the cells remain clinging together in the form of branching clusters.

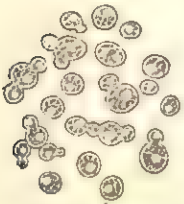


FIG. 49.—Yeast cells (highly magnified).

Theories of Fermentation.—Various theories have been advanced at different times to account for the chemical action of the living cells. Our knowledge of the subject is largely due to Pasteur, whose exhaustive researches have clearly shown that the decomposition of sugar is dependent on the life and growth of the yeast cell in the saccharine liquid. If the yeast is removed by filtration, or destroyed by boiling the liquid, fermentation ceases. Pasteur has described fermentation as life without air. According to his view, the yeast, deprived of air by immersion in the saccharine liquid, provides itself with the necessary oxygen from the sugar molecule, which is broken up in the act.

The recent researches of Buchner have, however, entirely modified our views on the whole subject of fermentation and other kinds of chemical change accomplished by living organisms. Buchner has shown that the contents of the dried and pulverised yeast cells may be extracted by great pressure, or by the aid of a solvent, and that the liquid so obtained, and freed by filtration from adhering cells, is capable of setting up fermentation like the living yeast. This substance he has termed *zymase*. Zymase is not, however, a single substance; for it contains at least two distinct compounds which may be separated by dialysis into the ferment and the co-ferment which passes through the dialyser. Neither of them alone can induce fermentation, but only when combined

(Harden). Fermentation is therefore merely a chemical process and the zymase which promotes fermentation is not an organism but a complex organic catalyst. Many such organic catalysts, which have not yet been produced except by living cells, are known and are called enzymes (p. 603).

Hydrolytic Enzymes.—When yeast is added to a solution of grape-sugar, $C_6H_{12}O_6$, fermentation soon begins; but if cane-sugar, $C_{12}H_{22}O_{11}$, is employed, the reaction is delayed. The difference is due to the nature of the two sugars. The cane-sugar is first resolved into two simpler sugars, viz. grape-sugar, or glucose, and fruit-sugar, or fructose, which are isomeric and which are both fermentable. This resolution or **hydrolysis** is effected by water, acting in the presence of another catalyst or enzyme, called *saccharase* or *invertase*, which is also present in yeast—

$$\underset{\text{Cane-sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Grape-sugar.}}{C_6H_{12}O_6} + \underset{\text{Fruit-sugar.}}{C_6H_{12}O_6}.$$

The same effect can also be catalysed by dilute solutions of sulphuric and hydrochloric acids, the process being called the *inversion of cane-sugar*, since the optical rotation of the solution becomes changed in sign (p. 305). Cane-sugar and glucose are both dextro-rotatory, whilst fructose is lævorotatory, but its lævorotation is greater than the dextrorotation of glucose, so that the final product rotates to the left.

Other enzymes.—We are acquainted with many enzymes, such as *diastase*, which occurs in leaves and germinating grain, and *ptyalin* in saliva, both of which convert starch into sugar; *pepsin*, in the digestive juices; *maltase* in malt, and many others. In general each enzyme promotes one specific reaction only—(Chapter XLII).

It is very probable that the bacteria—minute organisms which are responsible for a great variety of chemical changes among organic substances, such as the production of lactic and butyric acids from sugar and starch, and acetic acid from alcohol—contain a nitrogenous principle, like zymase, within the living cell, and that all these changes are purely chemical processes.

Manufacture of Beer, Wines, and Spirits.—In the manufacture of beer, barley is steeped in water and then spread in layers a few

inches deep on large floors where a steady temperature suitable for germination is maintained. During the process, the hydrolytic enzyme, diastase, is formed in the grain, and subsequently acts upon the starch present and converts it into sugar. After germination has proceeded for a few days, the grain is removed to a chamber where it is heated to a sufficiently high temperature to arrest germination, and at the same time to give the necessary flavour to the beer. The kiln-dried grain is called *malt*. It is now steeped in water at 60°–65°, when the diastase rapidly acts upon the starch, decomposing it into soluble dextrin and maltose, or malt-sugar, a sugar isomeric with cane-sugar, $C_{12}H_{22}O_{11}$. The extract, or *wort*, is then separated from the insoluble portion of the malt and run into large copper pans, where it is boiled with the addition of hops (the dried flowers of the plant), which impart a slightly bitter taste, and act at the same time as a preservative or antiseptic. The liquid from the pans is rapidly cooled and drawn into vats warmed to 15°–17°, and yeast is added. The maltose alone undergoes fermentation, and as this sugar constitutes only a small portion of the extract, the quantity of alcohol is not large. An additional quantity of alcohol is artificially introduced by adding glucose (p. 289) to the boiling pan. After fermentation has stopped, the liquid is run into casks and left to "brighten." The wort is capable of nourishing other micro-organisms besides the yeast plant, and if scrupulous cleanliness is not observed, or if impure yeast is used, lactic, acetic, and other fermentations may occur simultaneously, and produce what is known as the "diseases of beer," which show themselves in acidity, or in some other disagreeable flavour.

Wine is made from *must* or grape-juice, which contains grape-sugar. The juice is left in open vats and undergoes spontaneous fermentation, the quantity of alcohol depending upon the amount of fermentable sugar present. It is unnecessary for the wine-grower to add yeast as the brewer does, for the natural acidity of the must excludes foreign organisms. The yeast, necessary for fermentation, is derived from the dust, or bloom, which covers the outside of the grape.

Spirits, like whisky and gin, are also made from barley by a process which is nearly identical with that used in the brewing of beer. The main difference consists in the length of time during which the malt, or more frequently a mixture of malt and un-

malted grain, is steeped in water. During the limited time allowed for the diastase to act upon the starch in brewing beer, the starch is transformed into dextrin and into maltose. By the prolonged action of diastase, nearly the whole of the dextrin is converted into maltose, so that in the subsequent fermentation the maximum amount of alcohol is produced. Finally, the fermented liquor or *wash* is distilled and the alcohol redistilled or rectified.

If spirits of wine (ethyl alcohol) is required, the alcohol in the fermented liquid is concentrated by fractional distillation. The apparatus commonly used in this country is *Coffey's still*, which permits of the distillation being carried on continuously. The still is drawn in section in Fig. 50. It consists of a boiler, *a*, into which steam is admitted, and communicates with a column, *b*, called the *analyser*, and a second column, *c*, called the *rectifier*.

These columns are made of wood, and are lined with copper. The analyser is divided into compartments by horizontal plates of copper perforated with holes and furnished with valves opening upwards, and also with dropping tubes. The rectifier has a construction very similar to *b*. It receives the vapour passing from the analyser by the pipe *d*. The *wash* or fermented liquor is pumped into the zig-zag column of pipes within the rectifier *c*, which are heated by the surrounding vapours, and is finally discharged above the top of the perforated plate in the analyser *b* by the pipe *e*. Here it meets an ascending column of vapour from the boiler *a*, which deprives it of the more volatile alcohol. This alcoholic vapour undergoes further condensation in ascending the rectifier, so that on issuing from the pipe at the top of the rectifier it contains very little water, and is then condensed and collected. The *spent wash*, or liquid deprived of alcohol, collects in the boiler and is withdrawn from time to time by the waste pipe.

The spirit obtained in this way contains 95·6 per cent. of alcohol and 4·4 per cent. of water and is called *rectified spirit*. When diluted, and flavoured with various ingredients, it is sold as British brandy, British rum, etc. Rectified spirit boils at 78·13° C., which is only fractionally lower than the boiling-point of pure alcohol 78·3° C., but further concentration by fractionation is not possible since rectified spirit is a *constant boiling mixture* (p. 15). It is used for the manufacture of methylated spirit and many organic com-

pounds. In order to prepare pure alcohol from the rectified spirit made with Coffey's still, the liquid is filtered through charcoal, and is further fractionated. The first portions, or runnings, which contain aldehyde, and the last, known as *feints*, which consist of strong-scented fusel oil, are rejected. The alcohol is finally distilled over quicklime, and is sold as **absolute alcohol.** It still contains about a half per cent. of water, which can be removed by adding a quantity of metallic sodium or calcium and redistilling,

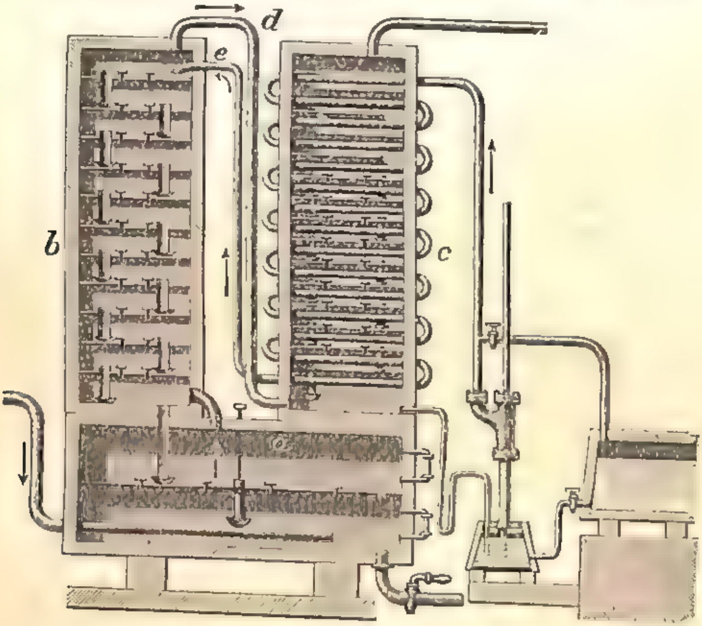


FIG. 50.—Coffey's still.

or by distilling a mixture of rectified spirit with benzene or certain other added liquids.

Alcohol is also manufactured, especially on the Continent, from potatoes and other materials, such as maize, rice, rye, oats, etc., which are rich in starch, and also by fermenting molasses or treacle, that is, the uncrystallisable portion of the sugar, and distilling the product.

Brandy or cognac is the alcoholic distillate from wine. Gin, like whisky, is made from barley, and flavoured with juniper; rum is the distillate from fermented molasses; hollands is prepared from

malt and rye. The following table gives the approximate percentage of alcohol contained in various fermented liquors :—

	Per cent.		Per cent.
Whisky	40	Burgundy	13
Brandy	40	Hock	9
Rum	40	Claret	7
Gin	35–40	Ale	6
Port	20	Porter	5–6
Sherry	16	Munich beer	4–5

Alcoholometry is the name given to the method of determining the quantity of alcohol in fermented liquors. All liquids containing alcohol, or made from alcohol, pay an excise duty which is extremely heavy. The old proof-spirit test was known as the *powder-test*, and consisted in pouring the liquid on to gun-powder, and then igniting it. If the alcohol contained so little water that it burnt away, leaving the powder dry enough to ignite, it was termed proof spirit; but if the powder was too damp to take fire, the spirit was under proof. The method which is now employed is to take the specific gravity of the liquid. Pure alcohol has a specific gravity of 0·806 at 0°, and 0·793 at 15°, and it would appear a simple matter to determine by calculation the quantity of alcohol in any mixture of water and alcohol. This cannot, however, be done so readily; because, when alcohol and water are mixed, there is a considerable contraction in volume.

Tables have been carefully compiled by Tralles, which give the quantity of alcohol corresponding to different specific gravities. The specific gravity is determined by a special form of hydrometer known as *Sikes's hydrometer*. The duty is levied on proof spirit which is defined by Act of Parliament as "such as shall at a temperature of 51° F. weigh exactly $\frac{12}{13}$ths part of an equal measure of distilled water." This corresponds to 49·3 per cent. by weight, or about equal weights of water and alcohol, or 57·09 per cent. by volume of alcohol. All spirit is estimated by its equivalent of proof spirit. Thus, every 100 gallons of spirit 25 over proof will be taxed as 125 gallons of proof, or 100 gallons of spirit 25 under proof will pay duty on 75 gallons of proof. It will be further observed, that the tax is payable on volume, not on weight, so that a standard temperature must be fixed upon to serve as a basis

for calculation. The standard temperature is taken at 51°F.

The Synthesis of Ethyl Alcohol.—Alcohol can now be manufactured from a product of the cracking of petroleum (p. 61). Ethyl hydrogen sulphate (p. 98), which was obtained by the interaction of alcohol and sulphuric acid, results also from the direct addition of fuming sulphuric acid to ethylene (p. 254)—

$$C_2H_4 + H_2SO_4 = C_2H_5HSO_4$$

and ethyl hydrogen sulphate when boiled with dilute sulphuric acid is hydrolysed again to alcohol—

$$C_2H_5H_2SO + H_2O = C_2H_5OH + H_2SO_5.$$

These last two reactions can now be effected simultaneously, so that ethyl alcohol results from the direct addition of water to ethylene. Under high pressure and high temperature the ethylene derived from the cracking of petroleum can be directly converted to alcohol.

Methylated Spirit.—Owing to the high duty on pure ethyl alcohol, methylated spirit is often used in its place. This is prepared from rectified spirit by adding to it crude wood spirit or other substances, which render it unpalatable. This process is called *denaturation*, and the purification of denatured spirit is extremely difficult. Two varieties of methylated spirit are used—viz., *mineralised methylated spirit* and *industrial methylated spirit*. The mineralised spirit contains about 9 per cent. of crude wood spirit and about 0·4 per cent. of petroleum naphtha, and is coloured with methyl violet. It becomes turbid when mixed with water, but it can be used as a fuel or in the manufacture of varnishes. It can be partly purified by distilling it over solid caustic potash, but the distillation without a licence is illegal. Industrial methylated spirit, on the other hand, contains only 5 per cent. of crude wood spirit and 95 per cent. of rectified spirit. It mixes freely with water, and can be used for a much greater variety of purposes—*e.g.*, for the manufacture of dyestuffs and fine chemicals. It is also used in surgery. For use in portable lamps a "solidified spirit" is made by dissolving soap in alcohol. On cooling, the solution sets to a solid mass, which is easily ignited. For scientific research industrial methylated spirit and rectified spirit can be obtained free of duty in certain institutions on application to the excise authorities.

Properties of Ethyl Alcohol.—Pure ethyl alcohol is a colourless liquid, with a burning taste and fragrant smell, and boils at 78°.

It burns with a blue flame, and is miscible in all proportions with water. The presence of small quantities of water in ethyl alcohol may be detected by adding anhydrous copper sulphate, which is turned blue, or by pouring a few drops into paraffin oil or benzene, which, if water is present, become turbid.

The usual test for ethyl alcohol is known as the **iodoform test.** A crystal of iodine or a little iodine solution is added to the liquid, together with a few drops of alkali, and the mixture is gently warmed. Crystals of iodoform will separate, which can be readily identified by their smell and by their crystalline form (p. 92). Acetone gives the same reaction as alcohol.

The following table gives a summary of the most important chemical changes which ethyl alcohol undergoes :—

REAGENT.	PRODUCT.
	The Halogens and Acids.
1. Chlorine; bromine.	Chloral, $CCl_3 \cdot COH$; **bromal,** $CBr_3 \cdot COH$.
2. Bleaching-powder and water.	Chloroform, $CHCl_3$.
3. Iodine and alkali.	Iodoform, CHI_3.
4. The halogen acids, HCl, HBr, HI.	Ethyl chloride, C_2H_5Cl; ethyl bromide, C_2H_5Br; ethyl iodide, C_2H_5I.
5. Bromine or iodine and red phosphorus.	Ethyl bromide; ethyl iodide.
6. Concentrated sulphuric acid.	Ethyl hydrogen sulphate, $C_2H_5HSO_4$; ethylene, C_2H_4; or ether, $C_4H_{10}O$.
7. Strong nitric acid.	Ethyl nitrate, $C_2H_5NO_3$.
	Oxidising Agents.
8. Potassium dichromate and sulphuric acid.	Acetaldehyde, $CH_3 \cdot CHO$.
9. Chromium trioxide.	The alcohol takes fire and burns to carbon dioxide and water.
10. Red hot platinum wire held in the vapour of alcohol.	Acetaldehyde, $CH_3 \cdot CHO$.
11. Platinum black and alcohol exposed to the air.	Acetic acid, $C_2H_4O_2$.

Propyl alcohol (propanol) is obtained from the fraction of fusel oil distilling at 97°, whilst *butyl alcohol* (butanol) is produced in

considerable quantities by a special fermentation process which converts starch (maize or rice is used) into a mixture of butyl alcohol and acetone (p. 143). Butyl alcohol is also present in fusel oil. It is used in conjunction with pyroxylins (see p. 313) in the preparation of lacquers.

Optical Activity.—Of the isomeric amyl alcohols, there are two present in fusel oil, viz. isobutyl carbinol, which is the chief constituent, and secondary butyl carbinol, which forms 10 to 20 per cent. of the mixture. The latter is also known as *active* amyl alcohol. The term active, which we shall frequently have occasion to use, has a special significance. It refers to the action which certain substances produce upon plane-polarised light.

When light passes through a crystal of calcite two refracted rays are produced, the ordinary and the extra-ordinary ray, each of which differs from ordinary light in being plane polarised. That means that the transverse vibrations of which each ray is composed are restricted to one plane only. A Nicol prism is cut from a crystal of calcite in such a way that only the extra-ordinary ray passes through it. This plane polarised ray will pass through a second Nicol prism in line with it, but only in certain positions. By rotating one of the prisms through a complete circle it will be found that at two positions, which are 180° apart, no light can pass through the combination. The Nicol prisms are then said to be "crossed." If we interpose a thin plate of quartz or a solution of sugar between crossed Nicols, light will again be transmitted, but it will be cut off again if we rotate one of the prisms through an angle, the magnitude of which depends on the thickness of the quartz plate or the amount of sugar solution traversed by the polarised light. An optically active substance is said to have the power of *rotating the plane of polarisation of light.* A substance is dextro-rotatory if the analyser has to be rotated in a clock-wise direction to extinguish the light. A careful distinction should be drawn between polarisation of light and "rotation of the plane" of light that has been polarised. The former effect is mostly produced by calcite. The rotation of the plane of polarisation is the property of certain crystals and of many organic compounds found in nature. Its study enables us to understand the structure of molecules.

A polarimeter (Fig. 51) consists essentially of two Nicol prisms in alignment, one of them, the polariser, being fixed; the other, the analyser, being mounted at the centre of a large revolving graduated circle provided with a vernier, so that very small angles may be measured accurately. An active liquid or solution is filled into an observation tube of known length, fitted at each end with a glass disc, held by screw caps. The tube is often enclosed in a jacket through which water at constant temperature is made to circulate. The tube is laid in a level

trough between the Nicol prisms and at the same height. It is necessary to use monochromatic light. Most of the older rotations have been made with the sodium flame, but the more powerful light of the mercury arc is more usual nowadays. This requires resolving with a spectroscopic eyepiece. The green line of wave-length $\lambda = 5461$ A.U. is the most suitable. It must be clearly understood that each spectral line will give a different reading with an optically active substance in the tube. A condensing lens is used to render the rays nearly parallel, and observations are made through a telescopic eyepiece. The position of the analyser is read on the vernier with crossed Nicols (*a*) without

FIG. 51.

the observation tube and (*b*) with the filled tube. The difference between the two readings is the observed rotation. It is very difficult to determine the position of complete extinction of the light, so that one has to use a supplementary device, not shown in the figure, called the "half-shadow device". This covers one half of the face of the polariser, so that the two halves of the field are extinguished at two different points, which are separated from one another by a very small angle. By moving the analyser backwards and forwards one can then observe the sudden change from darkness in one half to darkness in the other half. An intermediate position of uniform appearance is then easy to judge. It is called the "extinction," although, as a matter of fact, the field is not quite extinguished. But this sensitive point is much easier to find than the true extinction, and as the rotations are always obtained by differences, as already explained, no error is introduced.

Optical activity occurs in many naturally occurring compounds, such as sugar, sarcolactic acid, tartaric acid, turpentine, camphor, and nicotine, and is known to have a close connection with their molecular structure, for whereas quartz loses this property when its crystalline form is destroyed, organic compounds are optically active in solution, and in some cases even in the form of vapour. Pasteur's work in 1850 on the tartrates enabled Le Bel and van 't Hoff (1874) to associate optical activity with the presence in the molecule of an *asymmetric carbon atom*. Realising the necessity of representing the quadrivalent carbon atom in three dimensions, they adopted the regular tetrahedron for the purpose, and showed

that whenever four different groups are attached to the four corners, two different arrangements are possible (Fig. 52, I and II). These figures, in which *A*, *B*, *C* and *D* represent different groups, are not identical with one another, but are related as an object to its own mirror-image. Active amyl alcohol possesses such a configuration—

$$\begin{array}{c} CH_3 \\ | \\ C_2H_5—C—CH_2OH \\ | \\ H \end{array}$$

The two models in Figs. 52, I and II, represent *d*- and *l*-rotatory forms respectively, the inactive racemic compound being a mixture of both in equal quantities. Optical activity is often but not always associated with the presence of an asymmetric atom in the molecule. The subject is discussed more fully in Chapter XXIII.

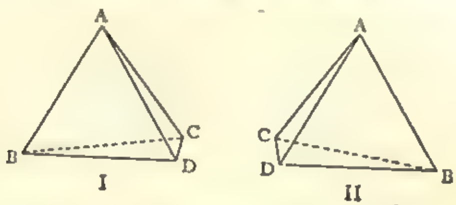


FIG. 52.

The Higher Alcohols.—The alcohols following amyl alcohol are termed *hexyl*, *heptyl*, *octyl* alcohol, etc., according to the number of carbon atoms in the molecule. The following alcohols are solid at the ordinary temperature:—*Cetyl alcohol*, $C_{16}H_{31}·OH$, which is combined with palmitic acid in spermaceti, a wax-like substance found in the head of the sperm whale; *ceryl alcohol*, $C_{26}H_{53}·OH$, found in combination with cerotic acid in Chinese wax. This wax is used in China for illuminating purposes, and collected from the bark of certain trees, where it is formed through the puncture of an insect; *melissyl* or *miricyl alcohol*, $C_{30}H_{61}·OH$, which is combined with palmitic acid in beeswax, and also occurs as a constituent of carnauba wax, a yellow brittle substance, found adhering to the leaves of the Brazilian palm.

Questions on Chapter VII

1. Why is methyl alcohol sometimes called *methyl hydroxide?*

2. Give equations representing the action of chlorine, hydrochloric acid, sodium, calcium chloride, and chromic acid mixture (potassium dichromate and sulphuric acid) respectively upon ethyl alcohol.

3. Give the formulæ for two primary, two secondary, and two tertiary hexyl alcohols and name them. Give also the formulæ and names of their products of oxidation.

4. How would you prepare a specimen of pure ethyl alcohol from grape-sugar? How is the purity of the alcohol ascertained?

5. Describe briefly the manufacture of beer, whisky, wine, and brandy. How is the amount of alcohol estimated in these liquids?

6. In what manner do the optical properties of certain organic substances give an indication of their structure?

7. Describe the manufacture of methyl alcohol. What impurity may it contain?

8. Give examples of *hydrolysis* produced by *enzymes*.

9. Discuss the meaning of the term *alkyl group*.

10. Give an epitome of the action of reagents on ethyl alcohol.

11. Name the following: $CH_3{\cdot}CH(OH){\cdot}CH_3$; $(CH_3)_2{\cdot}C(OH){\cdot}CH_3$; $(CH_3)_2{\cdot}CH{\cdot}CH(OH){\cdot}CH_3$; $(CH_3)_2{\cdot}C(OH){\cdot}C_2H_5$.

12. Give the modern explanation of the process of alcoholic fermentation. What are the chief products?

13. Describe the action of hydrochloric, nitric, and sulphuric acids on ethyl alcohol. Explain the application of the term *reversible* to these reactions.

14. By what processes would you prepare pure methyl alcohol from crude wood spirit?

15. Under what different conditions does sulphuric acid react with alcohol, and what products are formed in the several cases?

16. What are the principal chemical changes taking place (*a*) in a brewery, (*b*) in a distillery? What is methylated spirit?

17. How would you estimate the percentage of alcohol in a sample of wine?

18. What is "methylated spirit"? How would you proceed to detect methyl alcohol in the presence of ethyl alcohol?

19. What products are formed when primary and secondary propyl alcohols are gently oxidised? Compare and contrast their principal properties.

CHAPTER VIII

THE ETHERS

Physical and Chemical Properties of the Ethers.—The ethers have the same general formula as the alcohols, $C_nH_{2n+2}O$. A list of ethers is given in Table VII.

TABLE VII

THE ETHERS, $C_nH_{2n+2}O$.

		B.p.	Sp. gr.
Dimethyl ether	C_2H_6O	$-23{\cdot}6°$	—
Diethyl ether	$C_4H_{10}O$	$34{\cdot}6°$	0·731 (4°)
Dipropyl ether	$C_6H_{14}O$	$90{\cdot}7°$	0·763 (0°)
Di-isopropyl ether	$C_6H_{14}O$	69°	0·743 (0°)
Di-normal-butyl ether	$C_8H_{18}O$	141°	0·784 (0°)
Di-secondary-butyl ether	$C_8H_{18}O$	121°	0·756 (21°)
Di-isobutyl ether	$C_8H_{18}O$	122°	0·762 (15°)
Di-isoamyl ether	$C_{10}H_{22}O$	170°	0·799 (0°)
Di-normal-octyl ether	$C_{16}H_{34}O$	280°	0·805 (17°)
		M.p.	
Dicetyl ether	$C_{32}H_{66}O$	55°	—

Like the alcohols, they are colourless and neutral substances. When compared with the alcohols of the same molecular formula, they are seen to be much more volatile. Dimethyl ether, C_2H_6O, is isomeric with ethyl alcohol, but is a gas, which can be liquefied at $-23°$, whilst ethyl ether, $C_4H_{10}O$, which has the same molecular formula as butyl alcohol, boils at 34°. The ethers are specifically lighter than water, in which they are much less soluble than the alcohols. They offer a striking contrast to the alcohols in their chemical behaviour. Neither metallic sodium nor phosphorus chloride in the cold has any action on the ethers.

EXPT. 29.—Add a few thin slices of metallic sodium to 100 c.c. of ordinary ether contained in a distilling flask, cooled in water. Wait until the effervescence slackens, and then add more sodium until,

after a few hours, the addition of fresh sodium produces no further action. Then distil the ether from the water-bath. The distillate is now free from water. Add to one portion a small piece of sodium, and to another a little solid phosphorus pentachloride. In neither case will there be any perceptible action.

The ether with which chemists are most familiar is *diethyl ether,* commonly called **ether.** It will be taken as the representative member of the family. The discovery of ether is attributed

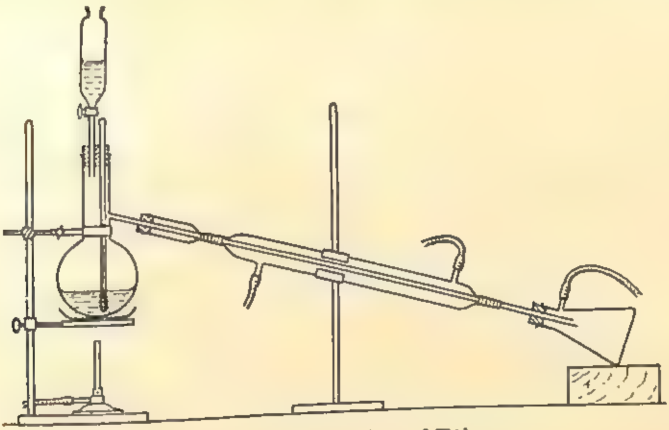


FIG. 55.—Preparation of Ether.

to Valerius Cordus in 1544. It was obtained by distilling pure spirits of wine with strong sulphuric acid. Boullay, early in the last century, found that the residue left in the retort after removing the ether, was able to furnish a fresh supply by the addition of more alcohol. This discovery originated the modern method of manufacturing ether, which is known as the **continuous etherification process.**

EXPT. 30. *Preparation of Ether.*—Fit up an apparatus like the one in Fig. 55. It consists of a distilling flask (½ litre) furnished with a tap-funnel and thermometer, the bulb of which is immersed in the liquid in the flask. The liquid consists of a mixture of 80 c.c. of concentrated sulphuric acid, and 110 c.c. of absolute alcohol. The flask is heated on a sand-tray and kept at a temperature of 140°, whilst fresh alcohol is allowed to drop slowly in from the tap-funnel. Ether and water collect in the receiver, which is cooled in ice or cold water. Since the

vapour of ether is heavier than air, the receiver should be fitted with a long piece of rubber tubing to conduct it to the floor, where it is not likely to come into contact with any flame. The distillate is purified by shaking it with a little dilute caustic soda to remove sulphurous acid, which is derived from a slight decomposition of the sulphuric acid. The caustic soda is drawn off, and a little strong solution of calcium chloride added to remove any alcohol which may be present. The salt solution is removed, and the ether first dehydrated over solid calcium chloride and finally over metallic sodium, as described in Expt. 29.

A small quantity of sulphuric acid can convert a very large amount of alcohol into ether, but the continuous formation of ether in this way presents some difficulty. As shown on p. 98, the alcohol reacts first with sulphuric acid to produce ethyl hydrogen sulphate, $C_2H_5HSO_4$, and water. When fresh alcohol acts upon the ethyl hydrogen sulphate at 130°–140° C. ethyl ether is formed and sulphuric acid is regenerated and is free to react with more alcohol. The usual equations are :—

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O$$

$$C_2H_5OH + C_2H_5HSO_4 = \underset{\text{Ether.}}{C_2H_5{\cdot}O{\cdot}C_2H_5} + H_2SO_4$$

The sulphuric acid should thus be able to convert an unlimited amount of alcohol into ether, but in practice this is not attained, since the acid becomes diluted by the water and some of it is reduced by carbonaceous by-products. The sulphuric acid combines, however, with water to a series of hydrates, which are progressively decomposed as the temperature rises, so that water is first held and then released by the acid. It has been found that loss of water begins at 120° C., and that at 140° C. the main reaction is the formation of ethylene. The best yield of ether is obtained at 136°–138° C., so that strict temperature control is essential. The addition of a small percentage of aluminium sulphate facilitates the formation of ether. Nevertheless after a time the reaction ceases and the process has to be interrupted. A continuous process has, however, been developed in which alcohol in the form of *vapour* is passed into a still containing a mixture of sulphuric acid and alcohol at 105° C., when the temperature rises to 128° C., and is maintained at that level by the heat of the reaction. When

methyl alcohol is used instead of ethyl alcohol no compound corresponding to ethylene is formed, so that the formation of dimethylether takes place more satisfactorily. By mixing one alcohol with sulphuric acid in the flask and running another into it during the heating, *mixed ethers* can be formed—*e.g.*—amyl ethyl ether $C_5H_{11}{\cdot}O{\cdot}C_2H_5$. Mixed ethers may also be prepared by the action on an alkyl iodide of a sodium alcoholate containing a different alkyl radical.

Metamerism.—The isomerism of similarly constituted compounds resulting from the combination of different radicals to the same multivalent atom or group is sometimes called metamerism, but the term is falling into disuse. Diethyl ether, $C_2H_5{\cdot}O{\cdot}C_2H_5$, is metameric with methyl propyl ether, $CH_3{\cdot}O{\cdot}C_3H_7$.

Constitution of Ether.—In 1851, Williamson synthesised ether by heating together sodium ethylate and ethyl iodide, and he afterwards prepared other members of the class by a similar process.

Expt. 31.—Dissolve 3 grams of sodium in 40 c.c. of pure alcohol contained in a flask attached to an upright condenser. When the sodium has dissolved, add 15 grams of ethyl iodide and heat the mixture on the water bath. In a few minutes a deposit of sodium iodide will be formed, and if the contents of the flask be distilled, ether and alcohol will collect in the receiver, from which the ether may be separated by the addition of salt solution.

Williamson's synthesis furnished the key to the structural formula of the ethers. We may explain the formation of methyl ether according to this synthesis as follows—

$$\begin{array}{ccccccccc} & H & & H & & H & & H & \\ & | & & | & & | & & | & \\ H— & C & —\boxed{I + Na}—O— & C & —H = H— & C & —O— & C & —H + NaI. \\ & | & & | & & | & & | & \\ & H & & H & & H & & H & \end{array}$$

Methyl-iodide. Sodium methylate. Dimethyl ether.

Dimethyl ether may be called *oxide of methyl*, just as methyl alcohol is called the hydroxide of methyl. The relation is that of sodium oxide to sodium hydroxide. Taking a general case, and representing the radical by R, the two parallel series of compounds will appear as follows—

R—O—H Alcohol.	R—O—R Ether.
Na—O—H Sodium hydroxide.	Na—O—Na. Sodium oxide.

The formula for ethyl ether is usually represented in one of the following ways—

$$\begin{array}{l} CH_3{\cdot}CH_2 \\ \qquad\quad \searrow O \\ CH_3{\cdot}CH_2 \nearrow \end{array} \qquad O\begin{array}{l} \nearrow C_2H_5 \\ \searrow C_2H_5 \end{array} \qquad \begin{array}{l} C_2H_5 \\ \quad\ \searrow O \\ C_2H_5 \nearrow \end{array} \qquad (C_2H_5)_2O.$$

Whichever formula is adopted, it must be clearly recognised that the characteristic group in the compound is the atom of oxygen linked on either hand to carbon, $\vdots C—O—C \vdots$. The above structural formula offers a ready explanation of the indifference of the ethers to sodium and phosphorus chloride. There is neither hydrogen nor hydroxyl to replace.

As the ethers are insoluble in water, the solubility of the lower alcohols in water must be attributed, not to oxygen alone, but to the hydroxyl group. The low boiling-point of the ethers, compared with the isomeric alcohols, is not exceptional. The substitution of hydrogen in a hydroxyl group by a radical frequently produces a lower-boiling product. Ethyl acetate, $C_2H_3O_2(C_2H_5)$, boils at 78°, whilst acetic acid, $C_2H_4O_2$, with nearly half the molecular weight, boils at 119°. Yet the only difference is the substitution of hydrogen in acetic acid for ethyl in ethyl acetate.

Ethers are very stable compounds and chemically rather inert, so that they are useful solvents, in spite of the fact that ether itself is very volatile and inflammable.

The character of the radicals composing the ether may be determined by heating the ether with strong hydriodic acid. The ether is decomposed into the corresponding alkyl iodides. Methyl propyl ether yields methyl and propyl iodides—

$$\begin{array}{cccccc} I & CH_3 & & CH_3I & & \\ H & & & & & \\ H & + O & = & + & & + H_2O. \\ I & C_3H_7 & & C_3H_7I & & \end{array}$$

Methyl propyl ether.

They may be separated by fractional distillation and identified by their boiling-points.

Properties of Ethyl Ether.—Ethyl ether is a very volatile and exceedingly inflammable liquid. It should therefore be kept away from a flame. Its vapour is very heavy, and forms with air an explosive mixture. It solidifies at $-117{\cdot}6°$.

EXPT. 32.—The density of ether vapour can be readily demonstrated by slightly tilting a beaker containing a little ether so that the vapour descends an inclined trough of cardboard. At the lower end a lighted burner is placed, and the vapour on reaching the burner is ignited, and the flame travels up the trough.

Ether, when inhaled, produces unconsciousness, and was introduced by Morton as an anæsthetic in 1846. It is also employed in the form of a spray, for producing local insensibility. The rapid evaporation of ether produces a low temperature, and this property is employed for refrigerating purposes.

EXPT. 33.—Pour a little ether into a beaker, and place it on a narrow board moistened with water. Blow a current of air through the ether by means of bellows for a few minutes. Hoar frost will form on the outside of the beaker, and the water below the beaker will freeze and fix it firmly to the board.

Ether is largely used as a solvent for resins, fats, oils, and alkaloids. It is frequently employed in the laboratory, for extracting oils from water, especially when the oil is disseminated through the water in fine particles. When ether is shaken up with such a liquid, it dissolves the oily globules and unites them in a layer on the surface of the liquid. This layer is easily separated from the water by a tap-funnel, and when the ether has been distilled off, the oil remains.

Methylated Ether is made like ethyl ether; but, in place of pure alcohol, methylated spirit is used. It is very impure, containing water, alcohol, and resinous matters. It may be purified by distilling it over solid caustic potash and then over sodium.

Preparation of pure ether.—Ether usually contains a little dissolved water and some alcohol and other products. For use as a solvent in ebullioscopic measurements and for Grignard reactions (p. 242) it is essential to use pure, dry ether. This is prepared by first washing it with small quantities of water, and, after separating the water, leaving the ether for a day or two in contact with dry calcium chloride to remove any alcohol as well as most of the water. The ether is decanted into a dry bottle and sodium wire is inserted. After a few days it will pass freely through a dry filter, and is now dry, but if it is at all coloured, it must be distilled from a water-bath and re-dried with sodium. A little sodium should be kept in it until it is wanted.

Questions on Chapter VIII

1. Describe the preparation and purification of diethyl ether by the *continuous process.*

2. How would you determine the constitution of a liquid, the molecular formula of which has been ascertained to be $C_5H_{12}O$?

3. Why is ordinary ether termed "ethyl oxide"?

4. Give two ways of preparing ethyl amyl ether from ethyl and amyl alcohols.

5. Explain and illustrate the term *metameric.*

6. What is the action of strong sulphuric acid upon ethyl alcohol?

7. How has the structure of ethyl ether been ascertained?

8. What is *methylated ether?* What impurities does it usually contain?

9. Write the constitutional formulæ for all the different bodies having the molecular formula $C_4H_{10}O$, and indicate by what experiments you would propose to distinguish them.

10. Explain the theory of the preparation of ordinary ether. What bearing has the mode of preparation on the constitutional formula of ether?

11. How is ethyl iodide made, and what is the action of sodium ethylate upon it? Point out the theoretical importance of this reaction.

CHAPTER IX

ALDEHYDES AND KETONES

A LIST of the more important aldehydes and ketones is given in Table VIII. It will be observed that the general formula of these substances is $C_nH_{2n}O$. They therefore contain 2 atoms of hydrogen less than the alcohols and ethers. The aldehydes (from *alcohol dehydrogenatum*) are obtained by the oxidation of the primary alcohols and the ketones by the oxidation of secondary alcohols (p. 101). There are other methods of preparation, which will be referred to later. The lowest member of the aldehydes is therefore the one obtained by the oxidation of methyl alcohol, viz., formaldehyde, CH_2O; the lowest ketone is prepared from secondary or iso-propyl alcohol, viz., dimethyl ketone, or acetone, C_3H_6O.

TABLE VIII.

ALDEHYDES, $C_nH_{2n}O$.

		B.p.
Formaldehyde	$H \cdot CHO$	—
Acetaldehyde	$CH_3 \cdot CHO$	21°
Propionaldehyde	$C_2H_5 \cdot CHO$	49°
Butyraldehyde	$C_3H_7 \cdot CHO$	74°
Isobutyraldehyde	$C_3H_7 \cdot CHO$	63°
Valeraldehyde	$C_4H_9 \cdot CHO$	102°
Isovaleraldehyde	$C_4H_9 \cdot CHO$	92°
Capronaldehyde	$C_5H_{11} \cdot CHO$	128°
Heptaldehyde, or Œnanthol	$C_6H_{13} \cdot CHO$	155°

KETONES, $C_nH_{2n}O$.

Acetone, or Dimethyl ketone	$CH_3 \cdot CO \cdot CH_3$	56°
Propione, or Diethyl ketone	$C_2H_5 \cdot CO \cdot C_2H_5$	103°
Butyrone, or Dipropyl ketone	$C_3H_7 \cdot CO \cdot C_3H_7$	144°
Isobutyrone, or Di-isopropyl ketone	$C_3H_7 \cdot CO \cdot C_3H_7$	125°
Isovalerone, or Di-isobutyl ketone	$C_4H_9 \cdot CO \cdot C_4H_9$	182°
Caprone, or Diamyl ketone	$C_5H_{11} \cdot CO \cdot C_5H_{11}$	227°
		M.p.
Œnanthone, or Dihexyl ketone	$C_6H_{13} \cdot CO \cdot C_6H_{13}$	30·5°

Constitution of Aldehydes and Ketones.—If phosphorus pentachloride is added to an aldehyde or ketone in the cold, an action ensues; but, although phosphorus oxychloride is formed, there is no evolution of hydrochloric acid. The action, therefore, differs from that of phosphorus chloride on the alcohols.

EXPT. 34.—Add gradually 10 to 15 grams of phosphorus pentachloride to 5 grams of acetone, cooled in water. The pentachloride dissolves, and the liquid turns yellow. Pour the product into ice-cold water, and let it stand until the phosphorus oxychloride has decomposed and dissolved. The heavy liquid which settles to the bottom, and smells like chloroform, is dichloropropane. The dichloropropane distils at 70°, and the distillate is purified like ethyl bromide (p. 81).

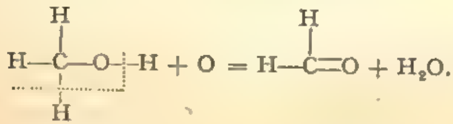
It is then found that the oxygen of the aldehyde or ketone has been replaced by 2 atoms of chlorine. No hydrogen is removed, and therefore no hydroxyl group is present as in the alcohols—

$$\underset{\text{Acetaldehyde.}}{C_2H_4O} + PCl_5 = \underset{\text{Ethylidene chloride.}}{C_2H_4Cl_2} + POCl_3$$

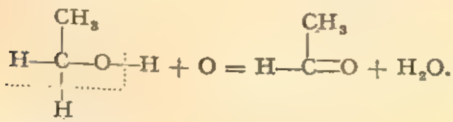
$$\underset{\text{Acetone.}}{C_3H_6O} + PCl_5 = \underset{\text{Dichloropropane.}}{C_3H_6Cl_2} + POCl_3$$

This reaction, and the fact that aldehydes and ketones are formed by the oxidation of alcohols, point to the existence of a $= C\dot{:}O$ group in both classes of compounds.

As the primary alcohols alone give aldehydes, the CO group must be present at the end of a carbon chain—

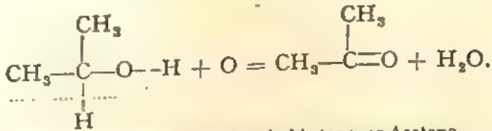


Methyl alcohol. Formaldehyde.



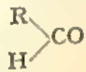
Ethyl alcohol. Acetaldehyde.

In the ketones, the CO group must be at another point of a carbon chain—

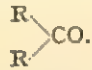


Secondary propyl alcohol. Dimethyl ketone, or Acetone.

The aldehydes are characterised by the group HC:O, which is called the *aldehyde group*, the ketones by C:O, which is termed the *ketone group*. The general formula for aldehydes and ketones, where R stands for the radical, is therefore represented as follows—



Aldehyde.



Ketone.

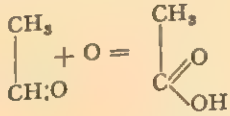
We shall see by the various reactions of aldehydes and ketones that the points of resemblance and difference are well expressed by this structural relation.

The action of phosphorus chloride on acetaldehyde and acetone can now be more correctly interpreted by the following equations—

$$CH_3{\cdot}CHO + PCl_5 = \underset{\text{Ethylidene chloride.}}{CH_3{\cdot}CHCl_2} + POCl_3.$$

$$CH_3{\cdot}CO{\cdot}CH_3 + PCl_5 = \underset{\text{Dichloropropane.}}{CH_3{\cdot}CCl_2{\cdot}CH_3} + POCl_3.$$

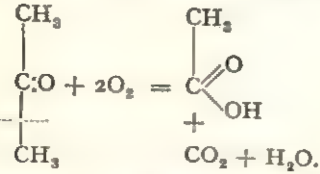
The general formulæ for aldehydes and ketones account, moreover, in a satisfactory manner for the fact that aldehydes can be oxidised without breaking the carbon chain, whereas the ketones usually lose both hydrogen and carbon in the process. Acetaldehyde gives acetic acid on oxidation; acetone decomposes into acetic acid and carbon dioxide[1] (p. 101)—



Acetic acid.

[1] These reactions are probably brought about through the intervention of water, and not by direct addition of oxygen—

$$CH_3CO{\cdot}H + H{\cdot}OH + O = CH_3COOH + H_2O.$$



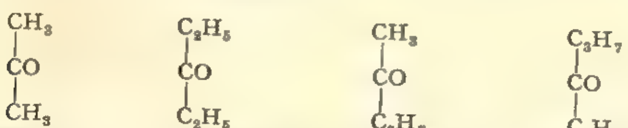
It should be noted that the rapidity with which oxidation occurs is much greater in the case of aldehydes (many of which undergo oxidation on exposure to the air) than with ketones, which are comparatively stable substances.

EXPT. 35.—Attach a half-litre flask to an upright condenser, and introduce 25 grams of potassium dichromate and 100 c.c. of dilute sulphuric acid. Boil the mixture, and drop into the boiling liquid from a tap-funnel, slipped into the top of the condenser, 10 c.c. of paraldehyde,[1] and continue to boil for about an hour. Distil half the contents, and neutralise the acid distillate with sodium carbonate. On evaporating on the water-bath, sodium acetate remains.

Nomenclature of Aldehydes and Ketones.—The aldehydes are either designated by the name of the alcohol from which they are derived or by the name of the acid to which they give rise on oxidation. The compound $H_2C{:}O$ is obtained by oxidising methyl alcohol, and is in turn converted by oxidation into formic acid. It is therefore known as meth(yl)aldehyde or form(ic)aldehyde, the syllable in brackets being omitted for brevity—

$$\underset{\text{Methyl alcohol.}}{CH_3OH} \longleftarrow \underset{\substack{\text{Methaldehyde,}\\ \text{or Formaldehyde.}}}{H_2CO} \longrightarrow \underset{\text{Formic acid.}}{HCO{\cdot}OH.}$$

The ketones are most simply described by the names of the radicals linked to the ketone group. They were originally named from the name of the acids, from which they were obtained by distillation (see below), joined to the end syllable "one." The following will serve as examples—



Dimethyl ketone, or Acetone. | Diethyl ketone, or Propione. | Methyl propyl ketone. | Dipropyl ketone, or Butyrone.

[1] Paraldehyde is more convenient to use for this experiment than acetaldehyde, which is so volatile that it escapes oxidation.

Diethyl ketone and methyl propyl ketone are metameric. On oxidation, the ketones break down between the radical and the ketone group. Thus, the division may and does occur at two points. For example, methyl propyl ketone yields, by the oxidation of the methyl group, butyric acid and carbon dioxide; by the oxidation of the propyl group, acetic and propionic acids, so that three acids are formed.

Preparation of Aldehydes and Ketones.—Where the corresponding alcohol is available, the common method of preparing aldehydes and ketones is to oxidise the alcohol with a mixture of potassium dichromate and sulphuric acid, or to pass the alcohol vapour mixed with hydrogen over finely divided copper heated to 300° (Sabatier). Although the aldehydes form acids on oxidation, the reverse process of reducing acids to aldehydes is not directly attainable. It may be effected, however, by the reduction of the acid chloride (p. 177) by hydrogen in presence of palladium, or by distilling a dry mixture of the calcium or barium salt of the acid with the same salt of formic acid.

The formation of acetaldehyde from calcium acetate and calcium formate may be represented as follows (ca′ = a half-atom of calcium)—

$$\begin{array}{r} CH_3\cdot CO\vdots Oca' \\ +\ H\vdots CO\cdot Oca' \end{array} \quad \text{or} \quad \begin{array}{l} CH_3\cdot\vdots CO\cdot Oca' \\ H\cdot CO\vdots Oca' \end{array} = CH_3\cdot CHO + CaCO_3.$$

The same reaction may be utilised for the preparation of ketones, provided some other organic acid be substituted for formic acid.

If calcium acetate be heated by itself, acetone is formed—

$$\begin{array}{r} CH_3\cdot CO\cdot\vdots Oca' \\ +\ CH_3\cdot\vdots CO\cdot Oca' \end{array} = CH_3\cdot CO\cdot CH_3 + CaCO_3.$$

If a mixture of two different calcium salts is taken, a ketone with two different radicals will be formed. Calcium acetate and calcium propionate yield methyl ethyl ketone—

$$\begin{array}{r} CH_3\cdot CO\vdots Oca' \\ +\ C_2H_5\vdots CO\cdot Oca' \end{array} = CH_3\cdot CO\cdot C_2H_5 + CaCO_3.$$

EXPT. 36. *Preparation of Acetone.*—Distil 30 grams of dry calcium acetate in a retort, attached to a condenser and receiver. The retort must first be warmed and then strongly heated. A light brown liquid collects in the receiver. The liquid consists of acetone mixed with

other products. By adding a few c.c. of a saturated solution of sodium bisulphite, a crystalline substance deposits on standing, which is a compound of acetone with sodium bisulphite. The acetone may be separated by distilling with sodium carbonate, but the quantity is usually too small for this purpose.

Another and similar method is to pass a mixture of acids over thorium oxide heated to 400° (Senderens)—

$$CH_3{\cdot}COOH + C_2H_5{\cdot}COOH = CH_3{\cdot}CO{\cdot}C_2H_5 + CO_2 + H_2O.$$

Other methods for preparing ketones will be referred to in subsequent chapters.

General Properties of Aldehydes and Ketones.—The chemical behaviour of these compounds depends upon two characteristic properties of the doubly linked oxygen of the C:O group: (1) the oxygen readily unites with the hydrogen of the reacting substance and passes into the hydroxyl group; (2) it is removed as water with hydrogen of the reacting substance. It is highly probable that the two processes are connected, and that the first always precedes the second.

Formation of the Hydroxyl Group.

(1) Aldehydes and ketones pass into alcohols on reduction—

$$>C{:}O + H_2 = >C<\begin{matrix}OH\\H\end{matrix}$$

Acetaldehyde, $CH_3{\cdot}CHO$, forms ethyl alcohol, $CH_3{\cdot}CH_2(OH)$; acetone, $CH_3{\cdot}CO{\cdot}CH_3$, gives secondary propyl alcohol, $CH_3{\cdot}CH(OH){\cdot}CH_3$.

In addition to the secondary alcohol, ketones form substances known as **pinacols**, by the union of 2 ketone molecules, with the addition of 2 hydrogen atoms. Acetone gives on reduction with sodium amalgam a pinacol of the following formula—

$$\begin{matrix}CH_3{\cdot}CO{\cdot}CH_3\\+\\CH_3{\cdot}CO{\cdot}CH_3\end{matrix} + H_2 = \begin{matrix}CH_3{\cdot}C(OH){\cdot}CH_3\\|\\CH_3{\cdot}C(OH){\cdot}CH_3\end{matrix}$$

Tetramethyl pinacol.

When pinacol is distilled with dilute sulphuric acid, rearrangement of the groups takes place, one of the methyl groups being transferred to another position—

(2) With hydrocyanic acid, an additive compound known as the **cyanhydrin** of the aldehyde or ketone is formed—

$$>C{:}O + HCN = >C\begin{matrix}\diagup OH \\ \diagdown CN\end{matrix}$$

Acetaldehyde gives acetaldehyde cyanhydrin, $CH_3{\cdot}CH(OH)CN$. Acetone forms acetone cyanhydrin, $CH_3{\cdot}C(OH)(CN){\cdot}CH_3$.

(3) A saturated solution of sodium bisulphite forms a crystalline additive compound with aldehydes and ketones. This can be readily shown by shaking up a little acetaldehyde or acetone with half the bulk of a saturated bisulphite solution.

The compounds are known as **bisulphite compounds** of the respective aldehyde or ketone, or as the sodium oxysulphonate of the radical.

$$>C{:}O + NaHSO_3 = >C\begin{matrix}\diagup OH \\ \diagdown SO_3Na\end{matrix}$$

Acetaldehyde forms $CH_3{\cdot}CH(OH)SO_3Na$, acetaldehyde sodium bisulphite, or ethyl oxysulphonate of sodium.

Removal of Oxygen as Water.

(1) With hydroxylamine, **oximes** are formed, which are known as *aldoximes* when derived from aldehydes, and *ketoximes* when prepared from ketones—

$$>C{:}O + H_2NOH = >C{:}N{\cdot}OH + H_2O.$$

Acetaldehyde forms acetaldoxime, $CH_3{\cdot}CH{:}NOH$; acetone yields acetoxime, $CH_3{\cdot}C{:}(NOH){\cdot}CH_3$.

EXPT. 37.—Mix together in a flask 5 grams of hydroxylamine hydrochloride dissolved in 10 c.c. of water, 3 grams of caustic soda in 10 c.c. of water, and 7 c.c. of acetone. Crystals of acetoxime soon begin to deposit, and the reaction is soon complete if cooled in ice, otherwise in a few hours.

(2) Hydrazine, $NH_2{\cdot}NH_2$, phenylhydrazine, $C_6H_5NH{\cdot}NH_2$,[1] and other derivatives of hydrazine react with aldehydes and

[1] The aromatic radical, C_6H_5, of benzene, C_6H_6, is called *phenyl*, and bears the same relation to benzene as ethyl, C_2H_5, to ethane, C_2H_6.

ketones with the removal of water forming **hydrazones, phenylhydrazones**, etc. (see p. 436)—

$$>C{:}O + H_2N{\cdot}NH{\cdot}C_6H_5 = >C{:}N{\cdot}NH{\cdot}C_6H_5 + H_2O.$$

EXPT. 38.—Add to a little phenylhydrazine rather more than an equal volume of glacial acetic acid and dilute the solution with two to three volumes of water. Mix the acetone with a little water, and add the solution of phenylhydrazine acetate. A turbid liquid results, which is due to the formation of acetone phenylhydrazone, an oily liquid insoluble in water. It may be extracted with ether by shaking and separating the ether with a tap-funnel. When the ether evaporates, acetone phenylhydrazone, $(CH_3)_2C{:}N{\cdot}NHC_6H_5$, remains. Bromophenylhydrazine, $C_6H_4BrNH{\cdot}NH_2$, and nitrophenylhydrazine, $NO_2{\cdot}C_6H_4NH{\cdot}NH_2$, used in the same way give crystalline products.

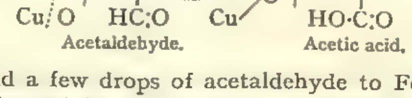
Aldehydes and ketones react with the Grignard reagents (p. 243) to give secondary and tertiary alcohols respectively.

Special Properties of Aldehydes.—Although the aldehydes share some of the properties of ketones, they differ from the latter in many important respects. They take up oxygen much more readily, forming acids, and are therefore active reducing agents. The aldehyde group is converted into what is known as a *carboxyl group*, $HO{\cdot}C{:}O$, about the structure of which more will be said in the following chapter on acids.

When an alkaline solution of a copper salt, such as Fehling's solution, is warmed with an aldehyde, the cupric oxide, which is present in solution, is reduced to cuprous oxide, and acetic acid is formed at the same time—

$$2CuO + C_2H_4O = Cu_2O + C_2H_4O_2;$$

or we may express the same reaction by structural formulæ—



Acetaldehyde. Acetic acid.

EXPT. 39.—Add a few drops of acetaldehyde to Fehling's solution and boil. A red precipitate of cuprous oxide is formed. Fehling's solution for qualitative tests is prepared by dissolving 3 to 4 grams of copper sulphate together with 5 to 6 grams of Rochelle salt in 50 c.c. of water. This is mixed, when required for use, with about an equal volume of caustic soda solution of 10 per cent. strength, when a clear

blue solution results. The Rochelle salt serves to keep the cupric oxide in solution, when alkali is added.

A similar reaction occurs with an ammoniacal solution of silver nitrate. This solution may be regarded as containing dissolved silver oxide. When a few drops of aldehyde are added to it and the liquid warmed, a metallic mirror of silver is deposited and acetic acid is formed.

EXPT. 40.—Add a few drops of acetaldehyde to half a test-tube of ammonia-silver nitrate solution, and place it in hot water. In a few minutes a mirror will cover the sides of the test-tube. The silver solution is prepared by adding dilute ammonia to silver nitrate until the precipitate of silver oxide just dissolves.

The aldehydes form a peculiar class of compounds with ammonia, known as **aldehyde-ammonias**. They are colourless, crystalline substances, formed by passing ammonia gas into an ethereal solution of the aldehyde (see Expt. 47, p. 139). The action takes place in the case of acetaldehyde as follows—

$$CH_3{\cdot}CHO + NH_3 = \underset{\text{Acetaldehyde-ammonia.}}{CH_3{\cdot}CH\left\langle\begin{matrix}OH\\NH_2.\end{matrix}\right.}$$

The aldehyde-ammonias give the reactions for aldehydes. They are soluble in water and easily decomposed by acids, ammonia being removed as the ammonium salt of the acid and the aldehyde is regenerated. Formaldehyde is an exception, and gives, with ammonia, *hexamethylene tetramine*, $(CH_2)_6N_4$, which is used medicinally under the name of *hexamine, aminoform* or *urotropine*

EXPT. 41.—To a few c.c. of formaldehyde solution (40 per cent.) add an equal bulk of conc. ammonia solution and evaporate on the water-bath. Colourless crystals of $(CH_2)_6N_4$ are deposited.

Caustic alkalis differ from ammonia in their effect upon aldehydes, the lower members of the series except formaldehyde being transformed into brown resin of unknown constitution.

EXPT. 42.—Boil a little acetaldehyde with caustic potash solution. The liquid soon becomes yellow, and eventually deposits a brown resinous substance known as *aldehyde resin*.

Formaldehyde reacts to give methyl alcohol and sodium formate, thus—

$$2CH_2O + NaOH = CH_3OH + H{\cdot}COONa$$

A further reaction for aldehydes is known as *Schiff's test*. If a little aldehyde is added to magenta solution, which has been rendered colourless with sulphur dioxide, a violet colour is produced.

EXPT. 43.—Make a dilute solution of magenta (fuchsine or rosaniline) in water, and bubble sulphur dioxide through it until the colour disappears. Add to the solution a few drops of aldehyde, and observe the violet coloration.

Two other reactions of aldehydes illustrate their characteristic properties.

When a solution of potassium carbonate is added to well-cooled acetaldehyde and the mixture left for some days, a syrupy liquid known as **aldol** [from ald(ehyde-alcoh)ol] is produced. It is a polymer formed by the union of two molecules of aldehyde—

$$CH_3{\cdot}CHO + CH_3{\cdot}CHO = \underset{\text{Aldol.}}{CH_3CH(OH){\cdot}CH_2{\cdot}CHO}.$$

Other aldehydes behave similarly. The process is usually referred to as the "aldol condensation" (p. 141), and, since aldol is itself an aldehyde, it can undergo further aldol condensation. Aldols readily lose water to form unsaturated aldehydes (p. 271). Warming with alkalis produces resins, due probably to a combination of these processes.

Aldehydes react with alcohols in the presence of a little dissolved hydrochloric acid gas or solid calcium chloride, forming compounds known as **acetals.** Formaldehyde reacts with methyl alcohol, giving *methylal*, $H_2C(OCH_3)_2$; acetaldehyde and ethyl alcohol yield *acetal*, $CH_3{\cdot}CH(OC_2H_5)_2$, from which the generic name of the class is derived. The reaction may be written as follows—

$$\underset{\text{Acetaldehyde.}}{CH_3{\cdot}CH\boxed{O + \begin{matrix} H \\ H \end{matrix}}}\underset{\text{Ethyl alcohol.}}{\begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix}} = \underset{\text{Acetal.}}{CH_3{\cdot}CH(OC_2H_5)_2} + H_2O.$$

Formaldehyde is obtained by the oxidation of methyl alcohol, by bringing the vapour, mixed with air, in contact with heated platinum or copper. If a red-hot spiral of platinum is suspended near the surface of methyl alcohol, the wire continues to glow,

and the acrid smell of formaldehyde is soon apparent. Oxidation takes place by means of the oxygen of the air, which is occluded, or absorbed, by the platinum, and is then in a much more active condition than free oxygen.

FIG. 56.

EXPT. 44.—Make a spiral of platinum wire by wrapping it round a glass rod, and leave one long end. Attach the long end to a short glass rod, which serves to suspend the spiral horizontally within a small beaker. Pour in methyl alcohol until the surface of the liquid rises to about one-eighth of an inch from the spiral. Gently warm the alcohol. Remove and heat the spiral red-hot, and replace it quickly. It will continue to glow, evolving formaldehyde. The arrangement of the apparatus is shown in Fig. 56. The above property of metallic platinum of glowing in the vapour of methyl alcohol and air is utilised in the form of cigar lighters, in which the alcohol is ignited by the red-hot metal.

In order to collect the formaldehyde, the vapour from the methyl alcohol, after passing a glowing platinum or copper spiral, is absorbed in alcohol or water.

EXPT. 45. *Preparation of Formaldehyde.*—The form of apparatus is shown in Fig. 57. The flask *a* contains about 50 c.c. of methyl alcohol. It is provided with a double-bored cork. Through one hole a glass tube passes to the bottom of the flask; and through the second a bent glass tube connects the flask with the short combustion tube *b*. Into the centre of this tube a loose plug of platinised asbestos is inserted, and kept in position by a short roll of copper gauze, which in turn is held in its place by a slight constriction of the tube. The platinised asbestos is prepared by soaking the loose fibrous asbestos in platinic chloride and gently igniting. The open end of *b* is attached, by a bent tube dipping to the bottom of the flask, to a flask, *c*, cooled in ice. A second tube, *d*, which terminates below the cork is joined to a water-jet aspirator. The flask *a* is warmed in a water-bath to about 40°, and a rapid current of air aspirated through the apparatus. The platinised asbestos is then heated until it begins to glow, after which the glowing will continue so long as the air current is sufficiently rapid. The liquid which condenses in the flask *c* is a strong solution of formaldehyde in methyl alcohol, and may be used in Expts. 41 and 43.

Solutions of formaldehyde, on evaporation *in vacuo*, or in the presence of a little concentrated sulphuric acid, yield a white,

amorphous powder, known as **paraformaldehyde,** which has the same percentage composition as formaldehyde, but it is probably a mixture of compounds of higher molecular complexity. On heating, it is volatilised and converted into formaldehyde vapour which condenses again as paraformaldehyde. The formula is therefore denoted by $(CH_2O)_n$. Formaldehyde, CH_2O, is a gas which liquefies at $-19{\cdot}2°$ and solidifies at $-118°$. Crude paraformaldehyde melts between 150° and 160° C. and contains a little water. Several crystalline compounds, melting at about 163° C., called polyoxymethylenes have also been obtained from the interaction of aqueous formaldehyde and concentrated sulphuric acid. They

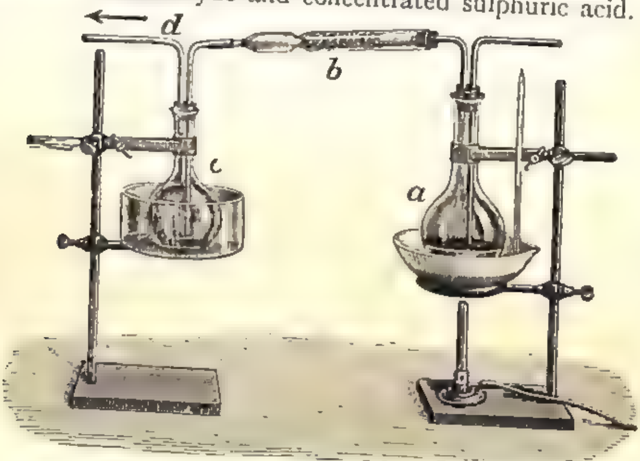


FIG. 57.—Preparation of Formaldehyde.

are also formed from formaldehyde vapour in contact with the vapour of formic acid. The polyoxymethylenes consist of long chains of CH_2O molecules linked at the two ends to hydrogen and hydroxyl, thus $H\text{–}[CH_2O]_n\text{–}OH$. By distilling paraformaldehyde or polyoxymethylenes into ice-cold water another crystalline compound, **trioxymethylene,** is formed, melting at 63° C. This compound does not give the characteristic aldehyde reactions and is known to have a cyclic structure.

Polymerisation.—Formaldehyde is said to undergo polymerisation in forming trioxymethylene. The latter is *polymeric* (πολύς, many; μέρος, a part) with, or a *polymeride* of, formaldehyde.

The term polymeric is used independently of the process of

polymerisation. It is sufficient for one substance to possess a multiple of the molecular weight of another to be polymeric with it, without any chemical relation existing between them. Acetic acid, $C_2H_4O_2$, is polymeric with formaldehyde, CH_2O, although the two compounds are chemically unconnected.

Technical Uses of Formaldehyde.—Since the introduction of formaldehyde as an antiseptic and disinfectant, and for other technical purposes, its manufacture is conducted on a commercial scale. Strong solutions, containing 40 per cent. of the aldehyde dissolved in water containing about 15 per cent. of methyl alcohol, known as *formalin*, as well as the solid paraformaldehyde, or *paraform*, are now sold. For disinfecting rooms, the solutions may be heated, or the solid paraform volatilised over a lamp. A convenient formaldehyde lamp may be constructed out of an ordinary spirit-lamp by surrounding the projecting wick with a ball of platinum foil and burning methyl alcohol. The lamp is lighted for a minute and then extinguished, when the platinum continues to glow, evolving formaldehyde.

As an antiseptic, a few drops of the solution will suffice as a preservative for a considerable quantity of material. About 30 milligrams of formaldehyde are sufficient to keep a litre of milk sweet for several days; but its use for this purpose is forbidden.

Formaldehyde has the property of rendering gelatine or glue insoluble in water. The aldehyde has in consequence been applied as a substitute for tannin in the leather industry. It has also been employed in a process for the production of artificial silk by exposing finely drawn out threads of glue to formaldehyde vapour, and for waterproofing with egg-albumin, which is then treated with the aldehyde. The effect of the aldehyde is readily observed by covering a piece of jelly made from gelatine or glue with formaldehyde solution, when on standing the gelatine no longer dissolves in water. Formaldehyde is also employed in the coal-tar colour industry. Large quantities are now required for the manufacture of plastic resins, which are hardened by heat. *Bakelite* (p. 461) is made from phenols and *beetle-ware* from urea and thio-urea (p. 341), by condensation with formaldehyde. It is also employed in the preparation of *iodoformin*—a compound of hexamine and iodoform—and of *formamint*, a substance composed of lactose and formaldehyde, and in the manufacture of synthetic tannins (p. 496).

In addition to the ordinary tests, formaldehyde may be detected when present in very minute quantities in a variety of ways.

EXPT. 46.—1. Add a drop of a 40 per cent. formaldehyde solution to 100 c.c. of water. To this solution add 2 c.c. of a 1 per cent. solution of phenylhydrazine hydrochloride and 1 c.c. of a 5 per cent. potassium ferricyanide solution. On adding a few drops of strong hydrochloric acid a rose-red tint is developed. 2. Dissolve about 0·1 gram of resorcinol in 3 c.c. of 20 per cent. caustic soda solution, add a drop of formaldehyde and boil. A brilliant red colour is developed.

One method for the analysis of formaldehyde solutions depends upon the formation of the compound $CH_2O{\cdot}KCN$ with potassium cyanide.

An excess of standard potassium cyanide is added to a dilute formaldehyde solution, and the excess then estimated by titrating with standard silver nitrate, using ammonium thiocyanate as indicator; or the aldehyde may be oxidised to formic acid by means of hydrogen peroxide in presence of excess of standard alkali, the excess being afterwards estimated—

$$CH_2O + H_2O_2 + NaOH = HCO{\cdot}ONa + 2H_2O$$

or by the use of iodine solution in which the excess of iodine is determined.

$$CH_2O + I_2 + H_2O = CH_2O_2 + 2HI.$$

Formose.—When a solution of formaldehyde is mixed with lime-water or magnesia at the ordinary temperature, it is slowly converted into a polymeric substance of the formula $(CH_2O)_6$ or $C_6H_{12}O_6$. The product is a sweet syrup, and its formula and many of its properties indicate a close relationship with grape- and fruit-sugar. It is known as *formose*. The fact has an interesting bearing on the production of the sugars by plants, which takes place during the assimilation of carbon dioxide by their chlorophyll, or green colouring-matter, in presence of sunlight. It has been suggested that in the process the carbon dioxide is reduced to formaldehyde, which then undergoes polymerisation. This view is supported by the observation that if carbon dioxide is passed into water containing colloidal uranium or ferric oxide or certain organic dyestuffs and exposed to sunlight or the light from a mercury-vapour lamp, formaldehyde may be detected. The conversion of a solution of the bisulphite compound of formaldehyde into starch by the living plant has also been observed.

Acetaldehyde is obtained from acetylene (p. 264), which is now a cheap commercial product, but is also prepared by the oxidation of ethyl alcohol with sodium dichromate and sulphuric acid. The following reaction occurs—

$$3C_2H_6O + Na_2Cr_2O_7 + 4H_2SO_4 = \underset{\text{Acetaldehyde.}}{3C_2H_4O} + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O.$$

EXPT. 47. *Preparation of Acetaldehyde.*—A flask of about 2 litres capacity is furnished with a double-bored cork. Through one hole a tap-funnel is inserted; and through the other a bent tube passes,

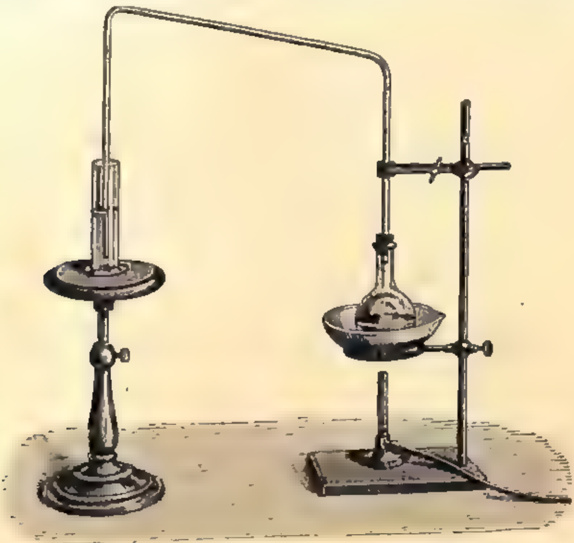


FIG. 58.—Preparation of acetaldehyde.

which connects the flask with a condenser and receiver. 100 grams of coarsely powdered sodium dichromate and 420 c.c. of water are placed in the flask, and a mixture of 125 c.c. of absolute alcohol and 75 c.c. of concentrated sulphuric acid is slowly run into the flask, which is warmed at the outset to start the reaction. Heat is developed in the process, and some aldehyde distils. When the alcohol and sulphuric acid have been added, the tap of the funnel is closed, and about 100 c.c. of liquid distilled, which contains most of the aldehyde mixed with alcohol and water. The aldehyde is next converted into aldehyde-ammonia.

For a rapid demonstration the following method may be used. The distillate is connected with a long tube, bent twice at an angle and dipping into a cylinder containing about 20 c.c. of ether (Fig. 58). The flask is gently heated in a basin of water, so that the aldehyde, which

boils at 21°, distils, leaving alcohol and water behind. After about a quarter of an hour the ether will contain a large quantity of aldehyde. This ethereal solution may either be saturated with ammonia gas, or a portion of it poured into a large round flask containing ammonia gas. In the latter case, the flask is closed loosely and shaken. The ammonia is soon absorbed, and if the stopper be now removed and the neck of the flask inclined so that the ether vapour can run out, crystals of aldehyde-ammonia will in a few moments cover the whole inner surface of the flask. The aldehyde-ammonia dissolves in water, and may be used for the tests given on pp. 132, 133. To obtain pure aldehyde, the aldehyde-ammonia is distilled with dilute sulphuric acid from the water-bath. The distillate is dehydrated over calcium chloride and redistilled—

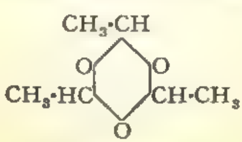
$$\underset{\text{Aldehyde-ammonia.}}{CH_3{\cdot}CH{<}^{NH_2}_{OH}} + H_2SO_4 = CH_3{\cdot}CHO + NH_4HSO_4.$$

Acetaldehyde is a colourless, pungent-smelling liquid, which dissolves readily in water and boils at 21°.

EXPT. 48.—It is readily detected by the addition of a few drops of sodium nitroprusside solution and piperidine when a blue colour is developed.

If a drop of concentrated sulphuric acid be added to a few c.c. of aldehyde, a vigorous reaction occurs and the liquid becomes hot and boils up. The product on adding water is no longer soluble. Polymerisation has taken place (p. 136) and **paraldehyde** has been formed. The same change occurs more slowly when acetaldehyde is kept for some time.

Paraldehyde is a colourless liquid boiling at 124°. It has the formula $(C_2H_4O)_3$. It is not an aldehyde, for it neither reduces silver oxide, nor combines with ammonia or sodium bisulphite. Its formula has been represented by a ring of alternate carbon and oxygen atoms, in which the oxygen atoms of the original aldehyde group serve as points of attachment for the 3 aldehyde molecules—



Paraldehyde.

It may be completely converted into acetaldehyde by distilling it with a little dilute sulphuric acid. Paraldehyde is used in medicine as a soporific. A solid compound, known as **metaldehyde,**

which is isomeric with paraldehyde, is obtained from acetaldehyde by the addition of hydrochloric acid gas, or dilute sulphuric acid, at a low temperature. It readily sublimes in light feathery crystals.

Acetaldehyde undergoes another kind of polymerisation, to which reference has already been made (p. 134). In presence of potassium carbonate two molecules of the aldehyde combine and form **aldol.** There is, however, a fundamental difference between paraldehyde and aldol. The latter cannot, like paraldehyde, be changed into the original aldehyde. It has therefore been classed in the category of reactions known as **condensations** (p. 143). The formation of aldol is represented as follows :—

$$CH_3{\cdot}CHO + CH_3{\cdot}CHO = \underset{\text{Aldol.}}{CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO}.$$

It is a hydroxybutaldehyde. It may be converted successively into crotonaldehyde (p. 271) and by hydrogenation into butyl alcohol

$$CH_3CH(OH){\cdot}CH_2{\cdot}CHO - H_2O = CH_3CH{:}CH{\cdot}CHO + 2H_2$$
$$\longrightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH.$$

Chloral, *Trichloraldehyde,* $CCl_3{\cdot}CHO$, is a substitution-product of acetaldehyde, although it is not obtained from the aldehyde by the direct action of chlorine. It was first obtained by Liebig in 1832 by passing chlorine into alcohol, and this is the method which is at present used in its manufacture. The reaction which occurs is not a simple one, and several by-products are formed. The principal product is a solid compound of chloral with alcohol, or *chloral alcoholate,* having the formula $CCl_3{\cdot}CH(OH){\cdot}OC_2H_5$. It bears a relation to the acetals (p. 134). A slow current of chlorine is first passed through cooled ethyl alcohol; later, the liquid is heated and the current of chlorine continued until no further absorption of the gas takes place. After cooling, chloral alcoholate separates, and is removed and distilled with concentrated sulphuric acid. Chloral passes over as an oily liquid, and is purified by shaking it with chalk to remove carbonyl chloride and hydrochloric acid.

The series of reactions is represented as follows :—

1. $CH_3{\cdot}CH_2OH + Cl_2 = \underset{\text{Acetaldehyde.}}{CH_3{\cdot}CHO} + 2HCl.$
2. $CH_3{\cdot}CHO + 3Cl_2 = \underset{\text{Chloral.}}{CCl_3{\cdot}CHO} + 3HCl.$
3. $CCl_3{\cdot}CHO + C_2H_5OH = \underset{\text{Chloral alcoholate.}}{CCl_3{\cdot}CH(OH){\cdot}OC_2H_5}.$
4. $CCl_3{\cdot}CH(OH){\cdot}OC_2H_5 + H_2SO_4 = CCl_3{\cdot}CHO + C_2H_5HSO_4 + H_2O.$

EXPT. 49.—Chloral may be obtained from chloral hydrate by distillation with conc. sulphuric acid. Distil 10 grams of chloral hydrate with 5 c.c. of conc. sulphuric acid in a small distilling flask and collect the colourless liquid distillate. On adding a few drops of water to 2–3 c.c. of the liquid, the solid crystalline hydrate is deposited.

Chloral is an oily liquid with a penetrating smell, and boils at 98°. It polymerises, like acetaldehyde, on keeping, or in presence of small quantities of mineral acids, and forms a white amorphous powder. On adding about one-fifth of its bulk of water and shaking, great heat is evolved and the mixture solidifies. The solid crystalline substance is **chloral hydrate,** and has the formula $CCl_3{\cdot}CHO + H_2O$, or more probably $CCl_3{\cdot}CH(OH)_2$. It dissolves readily in water, and, being much more stable than the liquid chloral, is the compound employed in medicine as a soporific. It gives some of the reactions of aldehydes, such as the reduction of ammonia-silver nitrate solution. It is most readily detected by its smell, and by the action of caustic alkalis, which, on warming, convert it into chloroform and sodium formate (p. 89)—

$$\begin{array}{c} H \\ | \\ NaO \end{array} + \begin{array}{c} CCl_3 \\ | \\ CHO \end{array} = \begin{array}{c} HCCl_3 \\ + \\ NaO{\cdot}CHO \\ \text{Sodium formate.} \end{array}$$

On boiling with strong nitric acid, chloral hydrate is oxidised to trichloracetic acid—

$$\underset{\text{Chloral hydrate.}}{CCl_3{\cdot}CH(OH)_2} + O = \underset{\text{Trichloroacetic acid.}}{CCl_3{\cdot}CO_2H} + H_2O.$$

By the action of potassium cyanide, or ferrocyanide, on chloral hydrate, dichloracetic acid is formed—

$$CCl_3{\cdot}CH(OH)_2 + KCN = \underset{\text{Dichloracetic acid.}}{CHCl_2{\cdot}CO_2H} + HCN + KCl.$$

The purity of chloral hydrate is a matter of great importance. It should give a clear solution with water, which must be free from acid and chlorine. Various compounds of chloral with other substances are employed as substitutes such, for example, as *dormiol*, a compound of chloral and amyl alcohol, and act in the same way as anodynes and hypnotics.

Bromal, $CBr_3 \cdot CHO$, is prepared like chloral, using bromine in place of chlorine. *Iodal*, $CI_3 \cdot CHO$, is also known.

Butyl chloral, $CH_3 \cdot CHCl \cdot CCl_2 \cdot CHO + H_2O$, is prepared by passing chlorine into paraldehyde and is a colourless solid. It is used as a soporific, having properties like chloral.

Acetone, *Dimethylketone*, $CH_3 \cdot CO \cdot CH_3$.—Boyle, in the *Sceptical Chymist*, describes the preparation of acetone from lead acetate by distillation. It is now manufactured together with a little methyl ethyl ketone by the dry distillation of calcium acetate, or by the action of acetic acid vapour on hot lime, also from crude wood-spirit by fractional distillation (p. 102). It is also produced together with butyl alcohol from maize and rice starch by a process of fermentation induced by an organism (*Fernbach's bacillus*) which converts the starch present into a mixture of about 2 parts of normal butyl alcohol and 1 part of acetone (p. 114). The acetone may be purified by adding sodium bisulphite solution and converting it into the crystalline bisulphite compound. This is filtered, pressed, and distilled with sodium carbonate—

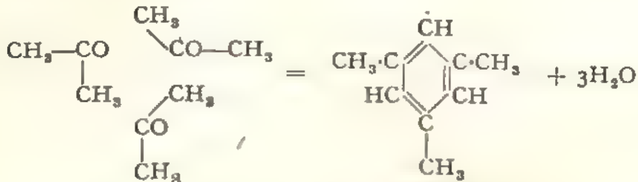
$$\underset{\text{Acetone sodium bisulphite.}}{2(CH_3)_2 \cdot C(OH) \cdot SO_3Na} + Na_2CO_3 = \underset{\text{Acetone.}}{2(CH_3)_2CO} + 2Na_2SO_3 + CO_2 + H_2O$$

The acetone passes over and is dehydrated over calcium chloride. It is finally distilled.

Acetone is sometimes present in the breath of diabetic patients. It is a colourless liquid with a fragrant smell, miscible with water; it boils at 56°. Its presence may be detected by the iodoform test (p. 113), which also serves for its quantitative estimation. A freshly prepared solution of sodium nitroprusside added to a dilute solution of acetone and then made alkaline with caustic soda gives a ruby-red colouration (Legal's test). The chief use of acetone is in the manufacture of chloroform and iodoform (pp. 90, 92), of sulphonal (p. 278), and as a solvent for nitrocellulose (celluloid, p. 314, and cordite, p. 288), and for acetylene gas. **Chloretone,** $CCl_3 \cdot C(OH)(CH_3)_2$, is a product formed from acetone and chloroform by the action of potash on the mixture, and is used as a specific against sea-sickness.

Condensation.—When acetone is mixed with twice its weight of moderately strong sulphuric acid and distilled, a liquid boiling at 163° passes over. This is *mesitylene*, or trimethyl benzene, C_9H_{12}

The action is represented by the removal of 3 molecules of water from 3 molecules of acetone.



Mesitylene.

The process is termed *condensation*, which has, however, nothing in common with the physical change of vapour to liquid. The word has a special meaning in organic chemistry, although its use is rather ill-defined. It generally implies the interaction of two or more molecules of the same or different substances, and sometimes of parts of the same molecule, usually, though not invariably, with the elimination of water, alcohol, or hydrochloric acid. The fundamental idea, which seems to be connected with the term, is that the new combination is effected by the union of carbon atoms, and is therefore of a stable character. In the formation of mesitylene water is eliminated; in the case of aldol nothing is removed in the process; yet in both cases carbon acts as the connecting link between the original molecules, and since the product cannot be readily broken up into its original constituents, the term condensation is applied to both reactions.

Questions on Chapter IX

1. Describe the preparation of pure acetaldehyde.

2. How would you distinguish between two substances having the formula C_3H_6O?

3. What is the action of sulphuric acid upon acetone and of hydrochloric acid upon acetaldehyde?

4. Give the characteristic reactions of the aldehydes.

5. How would you show that acetone contains 2 methyl groups attached to a CO group?

6. What are the oxidation products of ethyl propyl ketone?

7. Name the products of oxidation of primary and secondary propyl alcohol.

8. What is meant by the terms *polymerisation* and *polymeric?* What relation exists between the two?

9. Explain and illustrate the nature of *condensation*.

10. Give an account of the technical uses of formaldehyde. How is it prepared?

11. Describe the preparation of chloral hydrate. How is it converted into di- and trichloracetic acids?

12. How is formaldehyde best prepared? Give an account of its most striking and useful properties.

13. Give a list with formulæ of the so-called addition-compounds of aldehydes.

14. Describe how you would prepare a specimen of pure aldehyde, give an account of its physical properties, and enumerate as many reactions as you can in which it takes part.

15. What is meant by the terms: (*a*) addition-product, (*b*) substitution-product, (*c*) oxidation, (*d*) reduction, (*e*) polymerisation? Illustrate your answer by the reactions of ordinary aldehyde.

16. Give equations illustrating the preparation of chloral hydrate. Show by graphic formulæ its relation to aldehyde, and mention, giving an equation, its decomposition with caustic soda.

17. What are the chief characteristics of the ketones as a class? To what important changes do they lend themselves?

18. An organic compound is supposed to be a ketone. Explain precisely how you would prove experimentally that this is the case.

19. An aqueous solution contains either aldehyde, ethyl alcohol, or acetone. How would you distinguish the compound present?

CHAPTER X

THE FATTY ACIDS

MANY of the members of this group are constituents of animal fats and animal and vegetable oils, from which the name *fatty acid* has originated. The general formula of the fatty acids is $C_nH_{2n}O_2$, and they therefore contain an atom more oxygen than the aldehydes, or, compared with the alcohols, an atom of oxygen in place of two atoms of hydrogen. A list of the acids with their boiling-points and specific gravities is given in Table IX., on p. 148.

General Properties of the Fatty Acids.—They are colourless liquids or solids, the lower members possessing a sharp pungent smell and sour taste, which are absent among the higher members. As their names indicate, they are acids, and combine with bases to form salts. They are all monobasic, containing one replaceable hydrogen atom. If the electrical conductivity of an acid is taken as the measure of its strength,[1] the lowest member, formic acid, is twelve times as strong as acetic acid, after which there is a gradual diminution in the strength of the acids with increasing molecular weight. The solubility of the acids in water and their specific gravities also decrease. Formic acid has a specific gravity of 1·231, stearic acid of 0·845. Formic, acetic, propionic, and butyric acids mix in all proportions with water; but propionic and butyric acid separate from the solution on the addition of calcium or sodium chloride; isobutyric acid requires for solution 3 parts, and valeric acid about 30 parts of water. The higher members, though they dissolve in alkalis and form soluble sodium and potassium salts, are insoluble in water, and possess an oily or, if solid, a waxy consistency and are greasy to the touch. All the

[1] The electrical conductivity depends upon the number of free ions in the solution of the acid. The number of free ions is found to determine the chemical activity of the acid. Thus, an acid of the general formula R·COOH will dissociate into $R{\cdot}\overset{-}{C}OO$ and $\overset{+}{H}$, which according to the electronic hypothesis implies that hydrogen loses its electron and becomes a positive ion or proton, whilst the oxygen of the acid gains an electron and becomes the negative or anion. *Vide* J. Walker's *Introduction to Physical Chemistry* (Macmillan), chap. xxiv.

acids are soluble in alcohol and ether. It is somewhat curious that, among the higher members, those with an odd number of carbon atoms are rarely met with in nature, and also possess a lower melting-point than the next lower homologue with an even number of carbon atoms.

It will be seen from Table IX. that the boiling-points differ by about 20° between one member and the next in the series, formic acid having about the same boiling-point as water.

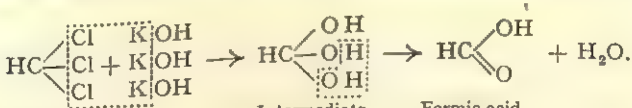
Constitution of the Fatty Acids.—A comparison of the boiling-points of corresponding paraffin, alcohol, aldehyde, and acid is instructive :—

Paraffin.	Alcohol.	Aldehyde.	Acid.
CH_4 (Gas)	$CH_3(OH)$ B.p. 66°	CH_2O B.p. −21°	CH_2O_2 B.p. 100°
C_2H_6 (Gas)	$C_2H_5(OH)$ B.p. 78°	C_2H_4O B.p. 21°	$C_2H_4O_2$ B.p. 118°

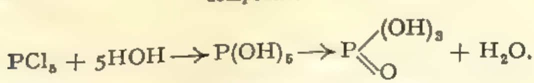
It will be noticed that the CO group in the aldehyde lowers the boiling-point below that of the corresponding alcohol. The rise of boiling-point in the acid affords strong evidence of the additional oxygen atom in the acid being present as hydroxyl.

We have already derived some knowledge of the structure of formic acid from previous reactions. It is formed by heating chloroform and iodoform with caustic alkalis (p. 92).

This change offers only one simple interpretation. The halogen is first replaced by hydroxyl, and the trihydroxy-compound, being unstable, loses the elements of a molecule of water in the same manner that phosphorus pentachloride yields phosphoric acid—



Chloroform. Intermediate compound. Formic acid.

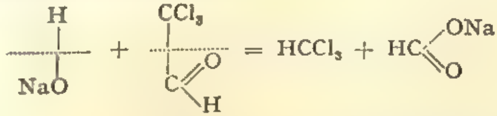


Phosphorus pentachloride. Intermediate compound. Phosphoric acid.

TABLE IX.—THE FATTY ACIDS, $C_nH_{2n}O_2$.

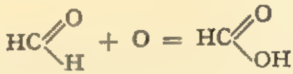
Acid.	Molecular Formula.	Structural formula.	Melting-point.	Boiling-point.	Sp. gr.
Formic	CH_2O_2	$H{\cdot}CO{\cdot}OH$	8·3°	101°	1·231 (10°)
Acetic	$C_2H_4O_2$	$CH_3{\cdot}CO{\cdot}OH$	16·5°	118°	1·052 (16·5°)
Propionic	$C_3H_6O_2$	$C_2H_5{\cdot}CO{\cdot}OH$	−24°	141°	1·013 (0°)
Butyric	$C_4H_8O_2$	$C_3H_7{\cdot}CO{\cdot}OH$	− 8°	162°	0·978 (0°)
Isobutyric	$C_4H_8O_2$	$(CH_3)_2CH{\cdot}CO{\cdot}OH$	−79°	154°	0·965 (0°)
Valeric	$C_5H_{10}O_2$	$C_4H_9{\cdot}CO{\cdot}OH$	−34·5°	185°	0·956 (0°)
Isovaleric	$C_5H_{10}O_2$	$(CH_3)_2CH{\cdot}CH_2{\cdot}CO{\cdot}OH$	−51°	174°	0·947 (0°)
Methylethylacetic	$C_5H_{10}O_2$	$(CH_3)(C_2H_5){\cdot}CH{\cdot}CO{\cdot}OH$	−80°	177°	0·941 (0°)
Trimethylacetic	$C_5H_{10}O_2$	$(CH_3)_3C{\cdot}CO{\cdot}OH$	35·4°	164°	0·905 (50°)
Caproic (Isobutyl acetic)	$C_6H_{12}O_2$	$(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2CO{\cdot}OH$	− 1·5°	200°	0·945 (0°)
Œnanthylic (Heptylic)	$C_7H_{14}O_2$	$C_6H_{13}{\cdot}CO{\cdot}OH$	−10·5°	223°	0·931 (0°)
Caprylic	$C_8H_{16}O_2$	$C_7H_{15}{\cdot}CO{\cdot}OH$	+16·5°	236°	0·927 (0°)
Pelargonic	$C_9H_{18}O_2$	$C_8H_{17}{\cdot}CO{\cdot}OH$	12·5°	186° (100 mm.)	0·911 (12°)
Capric	$C_{10}H_{20}O_2$	$C_9H_{19}{\cdot}CO{\cdot}OH$	31·4°	268°	0·930 (27°)
Undecylic	$C_{11}H_{22}O_2$	$C_{10}H_{21}{\cdot}CO{\cdot}OH$	28°	275°–280°	—
Lauric	$C_{12}H_{24}O_2$	$C_{11}H_{23}{\cdot}CO{\cdot}OH$	48°	225° At 100 mm.	0·875 At melting-point.
Tridecylic	$C_{13}H_{26}O_2$	$C_{12}H_{25}{\cdot}CO{\cdot}OH$	51°	236°	—
Myristic	$C_{14}H_{28}O_2$	$C_{13}H_{27}{\cdot}CO{\cdot}OH$	58°	250°	0·862
Isocetic	$C_{15}H_{30}O_2$	$C_{14}H_{29}{\cdot}CO{\cdot}OH$	55°	257°	—
Palmitic	$C_{16}H_{32}O_2$	$C_{15}H_{31}{\cdot}CO{\cdot}OH$	64°	271°	0·852
Daturic	$C_{17}H_{34}O_2$	$C_{16}H_{33}{\cdot}CO{\cdot}OH$	60°	227°	—
Stearic	$C_{18}H_{36}O_2$	$C_{17}H_{35}{\cdot}CO{\cdot}OH$	69°	383°	0·845
Arachidic	$C_{20}H_{40}O_2$	$C_{19}H_{39}{\cdot}CO{\cdot}OH$	77°	328°	—
Behenic	$C_{22}H_{44}O_2$	Unknown	84°	306° (60 mm.)	—
Lignoceric	$C_{24}H_{48}O_2$	,,	80°	—	—
Carnaubic	$C_{24}H_{48}O_2$	,,	72°	—	—
Hyænic	$C_{25}H_{50}O_2$	,,	77°	—	—
Cerotic	$C_{27}H_{54}O_2$	,,	82°	—	—
Melissic	$C_{30}H_{60}O_2$	,,	90°	—	—

Moreover, chloral decomposes rapidly and quantitatively into chloroform and sodium formate on warming with caustic soda, which clearly points to the same formula—

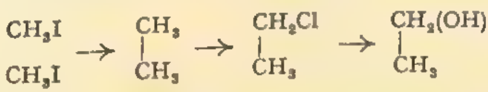


Chloral. Sodium formate.

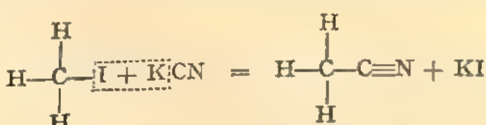
The formula also explains the production of formic acid by the oxidation of formaldehyde.



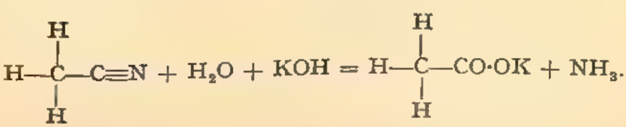
The Structure of Acetic Acid, $C_2H_4O_2$, is a more complex problem. The synthesis of ethane from methyl iodide and sodium (p. 72), its conversion into ethyl chloride, and the decomposition of the latter by potash into ethyl alcohol, prove the presence in the molecule of ethyl alcohol of two carbon atoms directly united—



The oxidation of alcohol to acetic acid would not disturb the union between the two carbon atoms, which must therefore be linked together in acetic acid. The direct union of two carbon atoms in acetic acid is proved, moreover, by the synthesis of the acid from methyl iodide and potassium cyanide. Methyl cyanide is formed, which readily yields the potassium salt of acetic acid together with ammonia on boiling with caustic potash solution—



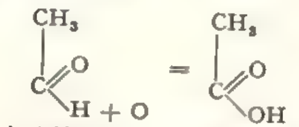
Methyl cyanide.



Potassium acetate.

Moreover when a solution of acetic acid is electrolysed (p. 153), the gas ethane is liberated at the anode along with carbon dioxide, so that we are justified in assuming the presence of a methyl group in the molecule of acetic acid.

We have therefore only to account for the grouping of the hydrogen and oxygen atoms round the one carbon atom. By analogy with the structure of formic acid in its relation to formaldehyde, acetic acid should, by a similar relation to acetaldehyde, possess the following constitution—



Acetaldehyde. Acetic acid.

Other evidence of the constitution of acetic acid may be briefly summarised as follows :—(1) The replacement of one hydrogen atom by a metal differentiates that hydrogen atom from the remaining three. (2) The replacement of one atom of hydrogen and one atom of oxygen simultaneously by one atom of chlorine when phosphorus pentachloride is allowed to act, indicates, by analogy with alcohol, the presence of a hydroxyl group (p. 96)—

$$C_2H_4O_2 + PCl_5 = C_2H_3OCl + POCl_3 + HCl.$$

(3) That this hydroxyl contains the replaceable hydrogen of the salts is shown by the action of chlorine on acetic acid. One, two, and finally three atoms of hydrogen are replaced by chlorine, forming the following three substitution-products in succession :—

$C_2H_3ClO_2$, Monochloracetic acid.
$C_2H_2Cl_2O_2$, Dichloracetic acid.
$C_2HCl_3O_2$, Trichloracetic acid.

All three compounds are acids, and form salts. It must be observed, however, that there is no direct evidence in the acid of the carbonyl group, CO, which is an unsaturated, highly reactive group in aldehydes and ketones, etc. Thus phosphorus pentachloride acts only on the hydroxyl group of acetic acid, and fails to react any further. Moreover, acetic acid possesses none of the properties characteristic of an unsaturated compound. It even resists oxidation by chromic acid, for which it is often used as a convenient solvent. Attempts have been made to devise an alternative structure for the carboxyl group, based upon the electronic structure of the atom (Chapter XXIV). Meanwhile, for the present, since methyl and hydroxyl groups have

both been proved to be present, we must be content with the structure already shown.

Thus, formic and acetic acid contain the same group $—CO{\cdot}OH$ united in the one case to hydrogen, in the other to the radical methyl—

$$\begin{array}{l} H \\ | \\ CO{\cdot}OH \end{array} \qquad\qquad \begin{array}{l} CH_3 \\ | \\ CO{\cdot}OH. \end{array}$$

Formic acid. Acetic acid.

In the same way the other homologues may be shown to be compounds of a radical united with the group

$$—C\begin{array}{l} \nearrow O \\ \searrow OH. \end{array}$$

This is known as the **carboxyl** group, and is the characteristic group of most organic acids.

Nomenclature.—The names of some of the acids are derived from the original sources of the acids, *e.g.* :—butyric acid, from butter; palmitic acid, from palm oil, etc. The higher members are usually denoted by Greek numeral prefixes.

The acid without the hydroxyl group forms a univalent group which has the properties of a radical, *i.e.* it is a constituent group of many compounds. This group is denoted by the general term **acid radical** or **acyl,** just as "alkyl" is the general term for the radical of the alcohols. The acyl like the alkyl radicals are used for convenience to denote certain groups, which do not exist as separate substances.

The following table contains the names of the first six acids, their derivation, and the names of the acyl groups :—

Name.	Derivation.	Acyl group.
Formic acid, $H{\cdot}CO{\cdot}OH$.	*formica*, an ant	formyl, $H{\cdot}C{:}O$
Acetic acid, $CH_3{\cdot}CO{\cdot}OH$.	*acetum*, vinegar	acetyl, $CH_3{\cdot}C{:}O$
Propionic acid, $C_2H_5{\cdot}CO{\cdot}OH$	πρῶτος, first; πίων, fat	propionyl, $C_2H_5{\cdot}C{:}O$.
Butyric acid, $C_3H_7{\cdot}CO{\cdot}OH$.	*butyrum*, butter	butyryl, $C_3H_7{\cdot}C{:}O$
Valeric acid, $C_4H_9{\cdot}CO{\cdot}OH$.	*Valeriana officinalis*, valerian	valeryl, $C_4H_9{\cdot}C{:}O$
Capric acid, $C_5H_{11}{\cdot}CO{\cdot}OH$.	*capra*, a goat	caproyl, $C_5H_{11}{\cdot}C{:}O$

Chemical Properties of the Fatty Acids.—The salts of the lower members of the fatty acids are, for the most part, soluble in water. The solubility of the salts diminishes with an increasing molecular weight of the acid. The salts of the alkalis are soluble in both water and alcohol.

In the formation of salts, the metal or metallic oxide interacts with the carboxyl group. Acetic acid and caustic soda form sodium acetate and water—

$$\underset{\text{Acetic acid.}}{CH_3\cdot C\begin{cases}O\\ O\boxed{H + HO}Na\end{cases}} = \underset{\text{Sodium acetate.}}{CH_3\cdot C\begin{cases}O\\ ONa\end{cases}} + H_2O.$$

In this respect the alcohols resemble the bases. **Esters** are thus formed (p. 182). Acetic acid and methyl alcohol form methyl acetate—

$$\underset{\text{Acetic acid.}\quad\text{Methyl alcohol.}}{CH_3\cdot C\begin{cases}O\\ O\boxed{H + HO}CH_3\end{cases}} \rightleftarrows \underset{\text{Methyl acetate.}}{CH_3\cdot C\begin{cases}O\\ OCH_3\end{cases}} + H_2O.$$

The process is reversible and slower than that with bases. The reverse action is called **hydrolysis.**

Phosphorus trichloride and pentachloride replace the hydroxyl group in the acid by chlorine. The substances thus formed are known as *acid chlorides* (p. 175). Acetic acid gives acetyl chloride—

$$CH_3\cdot C\begin{cases}O\\ OH\end{cases} + PCl_5 = \underset{\text{Acetyl chloride.}}{CH_3\cdot C\begin{cases}O\\ Cl\end{cases}} + HCl + POCl_3.$$

Chlorine gas produces substitution in the alkyl group, but has no action on the carboxyl group. Acetic acid forms chloracetic acid—

$$CH_3\cdot CO\cdot OH + Cl_2 = \underset{\text{Chloracetic acid.}}{CH_2Cl\cdot CO\cdot OH} + HCl.$$

Its action is accelerated by sunlight, or by the presence of a carrier such as red phosphorus, sulphur, or iodine. Bromine acts similarly, but iodine is without direct action. The action of

the halogens on the hydrocarbon radicals of the acids is therefore analogous to their behaviour with the paraffins (p. 64). The analogy may be carried further, for, like the alkyl halides (p. 83), the monohalogen derivatives of the acids exchange the halogen for other groups when acted upon with various reagents. Monochloracetic acid, for example, gives rise to the following products by the action of water, ammonia, and potassium cyanide respectively—

$$1.\ CH_2Cl{\cdot}COOH + H_2O = \underset{\text{Hydroxyacetic acid.}}{CH_2(OH){\cdot}COOH} + HCl.$$

$$2.\ CH_2Cl{\cdot}COOH + 2NH_3 = \underset{\text{Aminoacetic acid.}}{CH_2(NH_2){\cdot}COOH} + NH_4Cl.$$

$$3.\ CH_2Cl{\cdot}COOH + KCN = \underset{\text{Cyanacetic acid.}}{CH_2(CN){\cdot}COOH} + KCl.$$

The position of the halogen in the alkyl group of the higher fatty acids is generally denoted by lettering the carbon atoms α, β, γ, etc., beginning with the carbon to which the carboxyl group is attached. There are two, α and β, chloropropionic acids.

$$\begin{array}{ll} CH_3{\cdot}CH_2{\cdot}COOH, & \text{Propionic acid.} \\ \overset{\beta}{C}H_3{\cdot}\overset{\alpha}{C}HCl{\cdot}COOH, & \alpha\text{-Chloropropionic acid.} \\ CH_2Cl{\cdot}CH_2{\cdot}COOH, & \beta\text{-Chloropropionic acid.} \end{array}$$

It should be noted that by direct chlorination, or bromination, the halogen attaches itself to the α-carbon. The other halogen derivatives (β, γ, etc.) are obtained in a different manner (p. 270).

The behaviour of the fatty acids on electrolysis was first studied by Kolbe. He found that hydrogen is given off at the negative electrode, whilst a mixture of carbon dioxide and a paraffin is evolved from the positive electrode. Acetic acid yields ethane, carbon dioxide, and hydrogen. The reaction may be represented as follows :—

$$\begin{array}{ccccccc} & & \text{+Electrode.} & & & & \text{—Electrode.} \\ CH_3\text{—}COO\,H & & CH_3 & & CO_2 & & H \\ & = & | & + & & + & | \\ CH_3\text{—}COO\,H & & CH_3 & & CO_2 & & H \\ \text{Acetic acid.} & & \text{Ethane.} & & \text{Carbon dioxide.} & & \text{Hydrogen.} \end{array}$$

EXPT. 50. *Electrolysis of Potassium Acetate.*—As the pure acids are bad conductors, it is usual to take the potassium salt. A strong solution of potassium acetate is used. The apparatus (Fig. 59) consists of a porous cell, cemented to a wide glass tube, *a*. The cell is provided with a cork through which a platinum wire attached to a piece of platinum foil is inserted, which serves as the positive electrode. Through a second hole in the cork a delivery tube conducts the gases to a series of bulbs, *b*, containing potash solution which absorbs the carbon dioxide. The negative electrode consists of a platinum wire welded to a sheet of copper, placed in the outer vessel, *c*. Both vessels are filled with potassium acetate solution. On passing the current, hydrogen is evolved at the negative electrode and ethane and carbon dioxide at the positive electrode, the carbon dioxide being removed as the gases bubble through the bulbs. The ethane may be collected over water.

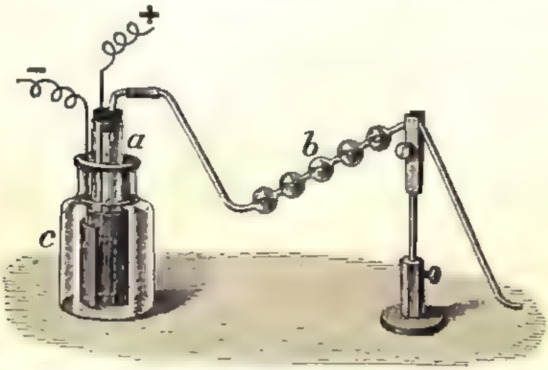


FIG. 59.—Electrolysis of Potassium acetate.

Before concluding the account of the properties of the fatty acids, the student is reminded of the behaviour of certain of the fatty acids on heating with soda-lime (p. 67), and of the products obtained by the distillation of their calcium salts (p. 129).

Sources of the Fatty Acids.—The fatty acids are found in combination with glycerol (glycerine) in fats and oils. Acetic and a little propionic acid are formed by the destructive distillation of wood, and a few of the lower members appear during the acid fermentation of alcohol and carbohydrates (starch, sugar, etc.). Formic, acetic, propionic, and butyric acids are formed in this way. Fatty acids are obtained by the oxidation of the alcohols (p. 100), and by the action of moderately strong sulphuric acid,

strong hydrochloric acid, or caustic alkalis on the alkyl cyanides. This reaction has already been referred to (p. 149). The process is an example of hydrolysis (p. 107), in which decomposition is effected by the addition of the elements of water. Methyl cyanide forms acetic acid and ammonia—

$$\mathrm{CH_3{\cdot}C}\boxed{\mathrm{N} + \begin{matrix}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{matrix}}\begin{matrix}\mathrm{OH}\\ \mathrm{O}\\ \ \end{matrix} = \mathrm{CH_3{\cdot}C}\begin{smallmatrix}\diagup\mathrm{OH}\\ \diagdown\mathrm{O}\end{smallmatrix} + \mathrm{NH_3}.$$

The presence of the acid or alkali accelerates the reaction by uniting in one case with the liberated ammonia and in the other with the free acid. There are many other methods for preparing the acids, which will be considered in subsequent chapters.

Methods for preparing Alcohols and Acids from Alcohols and Acids of a Different Series.—The above reaction offers a simple method for passing from one member of a series to the next. Methyl alcohol may be converted into the iodide, the cyanide, and finally, by hydrolysis, into acetic acid. On distilling calcium acetate with calcium formate, acetaldehyde is produced, which yields ethyl alcohol on reduction—

$$\mathrm{CH_3OH} \xrightarrow{\mathrm{HI}} \mathrm{CH_3I} \xrightarrow{\mathrm{KCN}} \mathrm{CH_3CN} \xrightarrow{\mathrm{H_2O}} \mathrm{CH_3{\cdot}COOH} \xrightarrow{\mathrm{HCO_2ca'}}$$
$$\mathrm{CH_3{\cdot}CHO} \xrightarrow{\mathrm{H_2}} \mathrm{CH_3.CH_2OH}.$$

The reverse process may be effected by distilling the alkali salt of the acid with soda-lime. Potassium acetate forms marsh gas, which may be converted into methyl chloride, methyl alcohol, and formic acid—

$$\mathrm{CH_3{\cdot}COONa} \xrightarrow{\mathrm{NaOH}} \mathrm{CH_4} \xrightarrow{\mathrm{Cl_2}} \mathrm{CH_3Cl} \xrightarrow{\mathrm{KOH}} \mathrm{CH_3OH} \xrightarrow{\mathrm{O_2}} \mathrm{HCO{\cdot}OH}.$$

Formic Acid, H·CO·OH, was obtained as early as the seventeenth century by distilling ants with water. It is present in stinging nettles and in the sting of bees. The methods by which the acid can be obtained are very numerous. We may refer to the action of alkalis on chloroform (p. 89) and chloral (p. 142) and to the oxidation of methyl alcohol (p. 100). Aqueous hydrocyanic acid is

hydrolysed on standing, yielding, among other products, ammonium formate—

$$\mathrm{HC}\boxed{\mathrm{N} + \begin{array}{r}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{array}}\begin{array}{l}\mathrm{OH}\\ \mathrm{O}\\ \end{array} = \underset{\text{Ammonium formate.}}{\mathrm{HCO{\cdot}ONH_4}}.$$

This is an example of the general method mentioned on p. 155. An interesting synthesis of formic acid was discovered by Berthelot, and consists in the direct union of carbon monoxide and caustic soda. The absorption takes place more rapidly if the gas is intro-

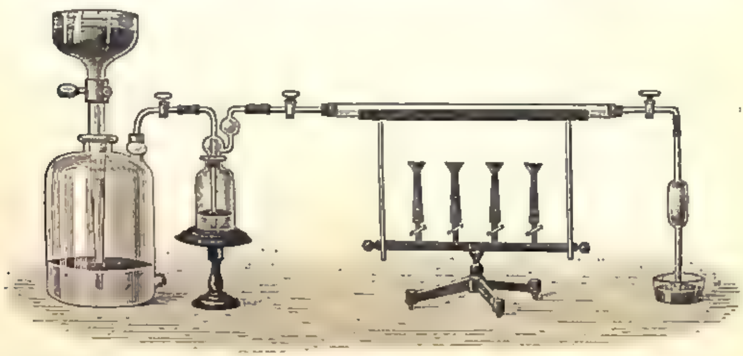


FIG. 60.—Synthesis of formic acid from carbon monoxide and soda-lime.

duced under pressure into a solution of sodium hydroxide at 160°, a method which is now utilised in its manufacture—

$$\mathrm{CO} + \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{ONa}\end{array} = \underset{\text{Sodium formate.}}{\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{ONa}\end{array}}$$

EXPT. 51.—An apparatus is fitted up as shown in Fig. 60. It consists of a tube of hard glass filled with soda-lime. One end is connected with a gas-holder containing carbon monoxide, the other with a pipette, dipping into coloured water. There is a glass tap at each end of the tube, which lies in a furnace, and is gently heated to a temperature of approximately 160°–170°. It is important not to raise the temperature too high. When the temperature has become constant, the tube is filled with carbon monoxide from the gas-holder. On shutting off the supply of carbon monoxide, by turning the tap, the coloured liquid

will rapidly ascend the pipette, indicating the absorption of the gas by the soda-lime.

Formic acid is found among the products formed by the oxidation of many organic substances, and represents the final stage before complete decomposition into carbon dioxide and water has been reached. The acid also appears during certain fermentative changes effected by the action of bacteria on the carbohydrates (sugars, starches, etc.) and alcohols.

Formic Acid from Oxalic Acid.—Formic acid is conveniently prepared in the laboratory by the decomposition of oxalic acid in presence of glycerol. Oxalic acid alone gives a small quantity of formic acid on heating—

$$\underset{\text{Oxalic acid.}}{C_2H_2O_4} = \underset{\text{Formic acid.}}{HCO_2H} + CO_2.$$

When glycerol is present, the reaction occurs in two steps. In the first, the acid oxalic ester of glycerol is formed and water separates. The structure of glycerol as trihydroxypropane and of oxalic acid as dicarboxyl must, for the present, be assumed.

$$\underset{\text{Glycerol.}}{\begin{array}{l} CH_2(OH) \\ | \\ CH(OH) \\ | \\ CH_2(OH) \end{array}} + \underset{\text{Oxalic acid.}}{\begin{array}{l} CO{\cdot}OH \\ | \\ CO{\cdot}OH \end{array}} = \underset{\text{Glyceryl oxalic ester.}}{\begin{array}{l} CH_2(OH) \\ | \\ CH(OH) \\ | \\ CH_2{\cdot}O{\cdot}CO{\cdot}CO_2H \end{array}} + H_2O.$$

The product breaks up into a compound known as *glycerol monoformin* and carbon dioxide. Fresh oxalic acid is now added, which hydrolyses the monoformin into glycerol and formic acid. The formic acid then distils. Each additional quantity of oxalic acid produces fresh formic acid, the glycerol being each time regenerated—

$$\begin{array}{l} CH_2(OH) \\ | \\ CH(OH) \\ | \\ CH_2O{\cdot}CO{\cdot}CO_2H \end{array} \rightarrow \underset{\text{Glycerol monoformin.}}{\begin{array}{l} CH_2(OH) \\ | \\ CH(OH) \\ | \\ CH_2O{\cdot}CH{:}O \end{array}} + CO_2 \rightarrow \begin{array}{l} CH_2(OH) \\ | \\ CH(OH) \\ | \\ CH_2(OH) \end{array} + HCO_2H.$$

The glycerol, in short, plays a similar part to that of sulphuric acid in the ether process (p. 129).

EXPT. 52. *Preparation of Formic Acid.*—Fifty grams of crystallised oxalic acid and 50 grams of glycerol are heated in a retort (250 c.c.) over wire-gauze, the retort being connected with condenser and receiver. A thermometer with its bulb in the liquid is fixed through the tubulus of the retort. The temperature is maintained at 105°–110° until the evolution of gas has slackened, and the liquid then distilled until the temperature reaches 120°. If a larger quantity of formic acid is required, 50 grams more of oxalic acid are added before distilling, and decomposition effected at 105°–110° as before. This process may be repeated. The distillate is boiled with excess of lead carbonate and filtered hot. On cooling, crystals of lead formate, $(HCO_2)_2Pb$, separate.

Pure formic acid is obtained by passing hydrogen sulphide over the dry lead salt heated to about 110°—

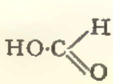
$$\underset{\text{Lead formate.}}{(HCOO)_2Pb} + H_2S = \underset{\text{Formic acid.}}{2H{\cdot}CO{\cdot}OH} + PbS.$$

The lead salt is contained in a wide tube plugged at each end with asbestos. The tube dips downwards so that the free acid runs down and collects in a receiver.

Properties of Formic Acid.—Pure formic acid boils at 101° and melts at 8°. It has a pungent and irritating smell and is extremely corrosive, raising blisters on the skin. All the salts are more or less soluble in water. Both acid and salts are decomposed with effervescence by concentrated sulphuric acid, yielding carbon monoxide. Pure carbon monoxide is readily obtained in this way. The reaction is easily shown by warming formic acid or a formate in a test-tube with strong sulphuric acid. On bringing a light to the mouth of the tube, the escaping gas ignites and burns with a blue flame. The sulphuric acid acts as a dehydrating agent—

$$HCOOH—H_2O = CO.$$

Formic acid and the formates are strong reducing agents. A solution of silver nitrate, when heated with the solution of sodium formate, gives a black deposit of metallic silver; mercuric chloride is reduced to the insoluble white mercurous salt, which is precipitated. This reducing action of formic acid, which distinguishes it from all the other fatty acids, is to be ascribed to the presence of the aldehyde group.



The compound may be described as a hydroxyaldehyde, which, like other aldehydes, is a reducing agent, and in turn undergoes oxidation to carbon dioxide and water—

$$HCOOH + O = CO_2 + H_2O.$$

When silver nitrate is added to a solution of sodium formate, the silver formate, which is first produced, decomposes into silver, carbon dioxide, and hydrogen. Part of the hydrogen is liberated in the free state, and a part reduces some of the silver formate, giving metallic silver and free formic acid—

$$\underset{\text{Silver formate.}}{2AgO{\cdot}COH} = Ag_2 + 2CO_2 + H_2.$$

We have seen that oxalic acid is converted into formic acid. The reverse process may be effected by heating dry sodium or potassium formate. The alkali salt of oxalic acid is produced, and hydrogen is at the same time evolved (p. 343). This process is now used in the manufacture of oxalic acid—

$$\underset{\text{Sodium formate.}}{\begin{array}{l} H\vdots CO{\cdot}ONa \\ \quad + \\ H\vdots CO{\cdot}ONa \end{array}} = H_2 + \underset{\text{Sodium oxalate.}}{\begin{array}{l} CO{\cdot}ONa \\ \vert \\ CO{\cdot}ONa. \end{array}}$$

Acetic Acid, $CH_3{\cdot}CO{\cdot}OH$, has long been known under the name of vinegar, and is produced when wine becomes sour. The name "acid" is derived from the Latin *acetum*, vinegar. Acetic acid was first prepared in the pure state in 1720 by Stahl, who noticed that its vapour was inflammable. If strong (glacial) acetic acid is boiled vigorously in a test-tube or flask, the vapour may be ignited as it issues from the mouth of the vessel, and burns with a blue, lambent, and very fugitive flame. Acetic acid is found in very small quantities in the juices of certain plants, in a few vegetable oils in combination with glycerol (see Oils, Fats, and Waxes, p. 166), and in some animal secretions. It is obtained by the hydrolysis of methyl cyanide (p. 155), and by the oxidation of ethyl alcohol, either by prolonged heating with potassium dichromate and sulphuric acid (p. 113), or by exposing the vapour of alcohol mixed with air to the action of platinum black. The platinum black acts like the platinum wire in Expt. 44, p. 135.

EXPT. 53.—Fill a tube about a foot long with platinised asbestos. The asbestos is prepared by soaking it in platinic chloride, and then heating it until it turns black. A wash-bottle, containing ethyl alcohol, is attached to one end of the tube, which is fixed horizontally. The alcohol is gently warmed, and a current of air bubbled through the alcohol, and then over the asbestos. Aldehyde and acetic acid are formed, the latter being readily indicated by holding a piece of blue litmus paper at the open end of the tube, when the paper soon turns red.

Acetic acid can be obtained directly or indirectly from acetylene, which is transformed successively into acetaldehyde and acetic acid, and the process is now used for its commercial production (p. 264). It is commonly prepared either from the pyroligneous acid obtained in the distillation of wood, or as vinegar by the **acetous fermentation** of alcoholic liquids.

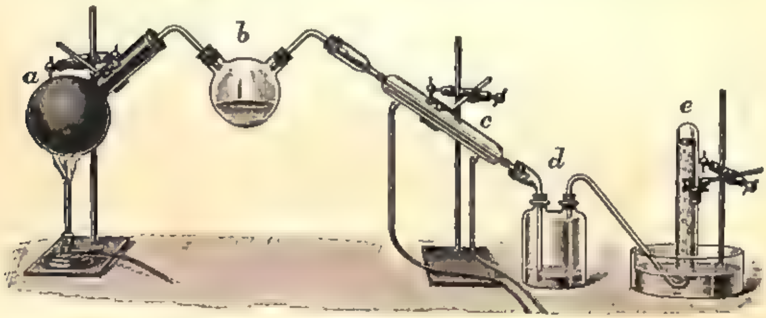


FIG. 61.

It has already been stated (p. 103) that in the destructive distillation of wood an aqueous distillate is produced, known as pyroligneous acid, containing acetic acid, methyl alcohol, and acetone.

EXPT. 54.—To illustrate the process the following apparatus may be used (Fig. 61). It consists of a copper retort or flask (*a*) containing dry saw-dust which is attached to a round flask with double tubulus (*b*). The latter is connected with a condenser (*c*) and a receiver (*d*) which consists of a bottle with a double neck. Through one tubulus of the receiver a bent tube attaches it to the condenser and through the other another bent delivery tube delivers the evolved gas to a cylinder (*e*) standing over water. The receiver contains caustic soda solution to absorb carbon dioxide. Tar and an aqueous distillate collect in the round flask and also in the receiver. The gas which collects in the cylinder is inflammable.

The aqueous distillate is neutralised with lime and the alcohol and acetone distilled off. The solution of the lime salt is evaporated, tarry and resinous matters being removed from the surface. The dry acetate of lime is gently heated to carbonise some of the impurities, and is then known as "grey acetate." It is distilled in copper vessels with strong hydrochloric acid sufficient to decompose the lime salt—

$$\underset{\text{Calcium acetate.}}{(CH_3{\cdot}COO)_2Ca} + 2HCl = \underset{\text{Acetic acid.}}{2CH_3{\cdot}COOH} + CaCl_2.$$

The distillate, which contains about 50 per cent. of acetic acid, is further purified by a second distillation over a little potassium dichromate. **Glacial acetic acid** is obtained by first converting the acid into the sodium salt by neutralising with soda. The sodium salt, $C_2H_3O_2Na + 3H_2O$, is then fused to expel the water of crystallisation, and then distilled with concentrated sulphuric acid. The pure acid solidifies on cooling, and forms a colourless, crystalline mass, from which the name *glacial* has originated. It melts at 16·7° and boils at 119°.

Fig. 62.—Vinegar Organism (*Mycoderma aceti*). Same magnification as yeast (p. 106).

Vinegar.—The souring of wine and beer when exposed to the air is due to the vinegar organism, mother of vinegar, or acetous ferment (*Mycoderma aceti*). It consists of cells constricted in the middle and often united in a chain (Fig. 62). The activity of the organism is prevented by strongly alcoholic liquids, such as spirits, port and sherry, and wines containing more than 15 per cent. of alcohol, which consequently do not turn sour. The methods used in the manufacture of vinegar are essentially alike. An alcoholic liquid, containing not more than 10 per cent. of alcohol is added to vinegar from a previous operation, containing the organism, and the liquid is freely exposed to the air. The organism acts as a carrier of oxygen between the air and the alcohol. In the manufacture of *malt vinegar*, the fermented wort, produced in the same manner as whisky, is poured into casks containing vinegar. The casks are aërated by leaving the bung-hole open and perforating the ends

near the top. When the transformation is complete, a portion of the vinegar is withdrawn, and the casks refilled with fresh liquor. *Wine vinegar* is made in the wine-growing districts of the Continent, and is produced from the poorer qualities of wine, in much the same manner as malt vinegar. It contains 6–8 per cent. of acetic acid, and owes its aroma to ethyl acetate and other substances present in the wine.

Quick Vinegar Process.—The vinegar generator or "graduator" is a large cask with two perforated discs of wood placed a little

FIG. 63.—Quick vinegar process.

distance from the top and bottom. Short threads are suspended through the holes in the top disc. To provide for the circulation of air, holes are bored in the sides of the cask above the lower disc. Birch twigs are packed in between the two discs (Fig. 63). The twigs are first covered with the mother of vinegar by pouring on strong vinegar. Weak spirit containing 5–7 per cent. of alcohol is slowly run in from the top and trickles over the twigs, in course of which the alcohol is converted into vinegar. The liquor runs out below, and having passed through a second time is finally clarified by running it over beech-wood shavings. The operation is conducted

so that a constant temperature of 35° is maintained within the cask. If too little air is admitted, acetaldehyde is formed. If oxidation becomes too active or too prolonged, the alcohol is oxidised to carbon dioxide and water.

Vinegar is never used in the preparation of pure acetic acid, which is entirely derived from pyroligneous acid and from synthetic acetaldehyde from acetylene (p. 264).

Properties of Acetic Acid.—Pure acetic acid is a useful solvent for organic substances. It is little affected by oxidising agents, and is frequently used as a solvent for chromium trioxide where a powerful oxidising agent is required. The addition of water to acetic acid produces a contraction in volume, so that an aqueous solution may have a higher specific gravity than the pure acid.

The volatility of acetic acid renders its detection a comparatively simple matter. The liquid to be tested is distilled, and the acid distillate neutralised with soda, and evaporated to dryness. On the addition of concentrated sulphuric acid, the strong smell of vinegar is at once apparent, or if a little alcohol is added before the addition of the sulphuric acid, the fragrant smell of ethyl acetate is observed—

$$CH_3 \cdot CO \cdot OH + C_2H_5OH = \underset{\text{Ethyl acetate.}}{CH_3 \cdot CO \cdot OC_2H_5} + H_2O.$$

Acetic acid is also detected by the red coloration which the solution of a neutral salt gives with ferric chloride. The red solution of ferric acetate loses acetic acid on boiling, and forms an insoluble basic salt. Similar reactions are given by formic acid; but acetic acid has no reducing action on silver and mercuric salts.

The Acetates.—Most of the normal salts of acetic acid are soluble in water. Lead acetate, or *sugar of lead*, $Pb(C_2H_3O_2)_2 + 3H_2O$, is obtained by dissolving lead carbonate in acetic acid. A solution of the normal salt dissolves lead oxide and forms *basic acetate of lead*.

Acetic acid is used in the manufacture of white lead, by exposing sheets of metallic lead to the combined action of acetic acid and carbon dioxide. *Verdigris*, or basic acetate of copper, $(C_2H_3O_2)_2Cu + Cu(OH)_2$, is used as a pigment, and is obtained by placing cloths dipped in vinegar in contact with sheets of copper. By

contact with the air, a crust of the basic acetate is formed on the surface of the copper, and is scraped off and ground up.

Schweinfurt green, $(C_2H_3O_2)_2Cu + (AsO_3)_2Cu_3$, is obtained by precipitating a solution of copper acetate with sodium arsenite, and is used as a pigment. *Iron liquor* and *red liquor* are solutions of the acetates of iron and aluminium, and used as *mordants* in calico printing and dyeing.

When the acetates, with which the cotton is impregnated, are heated, acetic acid is driven off, and the aluminium and ferric oxides remain firmly attached to the fibre, and fix the colouring matter with which the cloth is printed, or dyed. A substance which serves to attach colouring matter to cloth is termed a *mordant* (*mordre*, to bite).

Iron liquor is prepared by dissolving scrap iron in commercial acetic acid; red liquor is obtained by precipitating a solution of lead acetate with aluminium sulphate and filtering off the lead sulphate. The calcium salt of acetic acid is used in the manufacture of acetone (p. 143).

Substitution Products of Acetic Acid.—It has already been mentioned that when chlorine is passed into acetic acid, the hydrogen of the methyl group is replaced by chlorine. In this way mono-, di-, and tri-chloracetic acids are formed successively—

$$CH_3{\cdot}COOH + Cl_2 = \underset{\text{Monochloracetic acid.}}{CH_2Cl{\cdot}COOH} + HCl.$$

$$CH_2Cl{\cdot}COOH + Cl_2 = \underset{\text{Dichloracetic acid.}}{CHCl_2{\cdot}COOH} + HCl.$$

$$CHCl_2{\cdot}COOH + Cl_2 = \underset{\text{Trichloracetic acid.}}{CCl_3{\cdot}COOH} + HCl.$$

The action is promoted by sunlight, or by the presence of red phosphorus, sulphur, or iodine, which act as carriers. The chlorine is passed in, until the necessary addition in weight is obtained and the product is fractionated. Di- and tri-chloracetic acids are more conveniently obtained from chloral (p. 142). They are all colourless substances, mono- and trichloracetic acid being crystalline compounds, whereas dichloracetic acid is a liquid. The following are their melting- and boiling-points—

	M.p.	B.p.
Monochloracetic acid . . .	62°	185°
Dichloracetic acid . . .	—	190°
Trichloracetic acid . . .	52°	195°

Propionic Acid,—$C_2H_5 \cdot CO \cdot OH$, is most readily obtained by the oxidation of propyl alcohol with potassium dichromate and sulphuric acid. It accompanies acetic acid in pyroligneous acid, and is also found among the products of certain fermentation processes. Although it mixes with water, the acid may be separated from solution by the addition of calcium chloride. The acid then floats as an oily layer on the surface; for which reason it received the name of propionic acid (πρῶτος, first; πίων, fat).

Butyric Acid, $C_3H_7 \cdot CO \cdot OH$, occurs in two isomeric forms, both of which are found in nature. They may be obtained synthetically by one of the general methods already described.

Normal butyric acid was discovered in 1814 by Chevreul as a constituent of butter. It is present to the extent of about 7 per cent. as the glyceride, or glyceryl ester (p. 172). It occurs as the free acid in perspiration and in certain animal secretions.

The principal source of the acid is the fermentation known as the *butyric fermentation*, effected by the combined action of the lactic ferment and the *Bacillus amylobacter*, consisting of slender rods in active movement, on sugar, starch, and other carbohydrates.

A solution of starch or glucose is prepared, and putrid cheese, sour milk, and chalk, or zinc carbonate, together with a little tartaric acid, ammonium phosphate, and magnesium sulphate, are added, the temperature being maintained at 35°–40°. The cheese and sour milk contain the ferments, and at the same time supply nutrient albuminoid matter for the growth of the organisms, to which the tartaric acid and inorganic salts also contribute; the carbonate neutralises the free acid formed in the process, which, if allowed to accumulate, would arrest fermentation.

This process takes place in several stages. If starch is employed, it is first converted into glucose. The glucose then forms lactic acid (p. 322), and finally the lactic acid decomposes into butyric acid—

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = \underset{\text{Lactic acid.}}{2C_3H_6O_3}.$$

$$2C_3H_6O_3 = \underset{\text{Butyric acid.}}{C_4H_8O_2} + 2CO_2 + 2H_2.$$

Other changes also occur, and at the same time acetic, caproic, and caprylic acids are formed.

The solution of the calcium or zinc salt obtained in the above process is filtered, evaporated, decomposed with hydrochloric acid, and the butyric acid separated by steam distillation and redistillation.

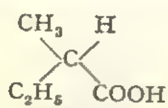
Butyric acid is a liquid with the smell of perspiration and of rancid butter. The disagreeable smell which rancid butter emits is usually attributed to free butyric acid produced by the action of certain micro-organisms.

Butyric acid is used in the manufacture of certain alkyl salts, or esters, which are employed for flavouring essences (p. 188).

Isobutyric acid has not been observed in any process of fermentation: but is found either as the free acid or ester in many plants.

EXPT. 55.—A simple method for distinguishing butyric and isobutyric acids is by means of their calcium salts, that of butyric acid being only slightly soluble in hot water, but soluble in cold water, whereas calcium isobutyrate shows the reverse phenomenon. If therefore a hot saturated solution of the isobutyrate and a cold saturated solution of the butyrate be prepared, the first will deposit crystals on cooling. If the two solutions are now placed in hot water the isobutyrate will dissolve and give a clear solution and the butyrate will deposit crystals.

Valeric Acid, *Valerianic acid*, $C_5H_{10}O_2$, is known in four isomeric modifications. Two of the isomerides, isovaleric or isopropyl acetic acid, $(CH_3)_2\cdot CH\cdot CH_2\cdot COOH$, and methyl ethyl acetic acid, $(CH_3)(C_2H_5)CH\cdot COOH$, are obtained by the oxidation of the amyl alcohol of fusel oil. Isovaleric acid occurs as the glyceride in certain blubber oils. The two acids are found together in valerian root and in angelica, from which they may be removed by distilling with water. They are oily liquids, only slightly soluble in water. Methylethyl acetic acid is optically active and contains an asymmetric carbon atom (p. 115). It is sometimes known as active valeric acid—



Active valeric acid.

Oils,[1] Fats, and Waxes.—The nature of these substances was first correctly described by Chevreul (1815–1823), who showed that

[1] The term oils used in the present sense implies the vegetable, non-volatile, or *fixed oils*, which must be carefully distinguished from the very different class of volatile, or *essential oils* (Part II. p. 506).

they were compounds of fatty acids with glycerol. Beef and mutton tallow and lard consist chiefly of the glycerides of stearic acid (στέαρ, tallow), $C_{18}H_{36}O_2$, palmitic acid, $C_{16}H_{32}O_2$, and oleic acid, $C_{18}H_{34}O_2$. Oleic acid is not strictly a member of this series of fatty acids. It is called an *unsaturated* fatty acid, as it contains 2 atoms of hydrogen less than stearic acid, which is a *saturated* acid (p. 271); but it is convenient to include it here. The glycerides, as they occur in fat, are known as *stearin* and *palmitin* (75 per cent.), which are solids, and *olein* (25 per cent.), which is liquid at the ordinary temperature. At the body temperature all the fats are liquid—

$$\begin{array}{l} C_{17}H_{35}CO{\cdot}O{\cdot}CH_2 \\ \qquad\qquad\qquad\;| \\ C_{17}H_{35}CO{\cdot}O{\cdot}CH \\ \qquad\qquad\qquad\;| \\ C_{17}H_{35}CO{\cdot}O{\cdot}CH_2 \end{array}$$

Formula of Stearin, the glyceride of stearic acid, or glyceryl stearate.

These substances are, however, not confined to the animal fats. Palmitin is the chief constituent of palm oil, olein of olive oil, of which it constitutes 75 per cent., whilst stearin is frequently found in animal and vegetable oils. Butter and cocoa-nut oil contain, in addition to the above, *butyrin*, the glyceride of butyric acid, $C_4H_8O_2$, whilst butter also contains the glycerides of caproic acid, $C_6H_{12}O_2$, caprylic acid, $C_8H_{16}O_2$, and capric acid, $C_{10}H_{20}O_2$. The three molecules of acid radical present in the fat are not necessarily the same and certain fats, such as butter fat, may contain three different acid radicals. It is difficult to draw any chemical distinction between oils and fats. They consist mainly of glycerides of saturated fatty acids; but the acid may belong, like oleic acid, to a different series. Linseed oil contains the glyceride of linoleic acid, $C_{18}H_{32}O_2$, which has less hydrogen than oleic acid (p. 272). In the waxes the glycerol is replaced by a higher alcohol of the methyl alcohol series, like cetyl alcohol, $C_{16}H_{33}(OH)$, which is combined with palmitic acid in spermaceti.

The analysis of oils, fats, and waxes is technically of great importance, and forms a special branch of commercial analysis, which cannot be described here.[1] The *saponification value*, or amount of alkali required to neutralise the fatty acids in a given

[1] Vide *Oils, Fats, and Waxes* (II. Ed.), Lewkowitsch. (Macmillan.)

weight of oil or fat, is estimated by heating a weighed amount of the substance with a standard solution of alcoholic potash, an excess of which is taken. The fatty acids unite with the alkali, and form the potassium salts. The excess of alkali, and consequently the quantity of alkali required for neutralisation of the fatty acid, is ascertained by titration with standard hydrochloric acid. The *iodine value*, or amount of iodine absorbed, gives a measure of the amount of unsaturated acids present, these substances possessing the property of forming additive compounds with iodine (p. 247). A number of separate estimations of both physical and chemical characters is needful to arrive at a correct knowledge of the fats and oils, which are, as a rule, very complex mixtures.

Saponification is a special case of hydrolysis (p. 107). The term is applied to the breaking up of an ester into its two constituent parts, the alcohol and the acid, by the addition of the elements of water. To take a simple case, the hydrolysis of methyl formate gives methyl alcohol and formic acid, and may be represented by the following equation :—

$$\begin{array}{ll} \text{Methyl formate.} & H{\cdot}CO{\cdot} \vdots OCH_3 \\ & \quad + \qquad\qquad = HCO{\cdot}OH + CH_3OH \\ \text{Water.} & \quad HO \vdots H \qquad\quad \text{Formic acid.} \quad \text{Methyl alcohol.} \end{array}$$

The decomposition can be effected in some cases by water, in others by a solution of caustic alkalis, or again by sulphuric acid.

Manufacture of "Stearine" Candles.—The so-called "stearine" used in the manufacture of candles is not glyceryl stearate, to which the name is usually applied, but the free acids from fat, separated as far as possible from oleic acid. The production of these acids from fat illustrates the variety of reagents which may be employed in saponification. The old process was to heat the fat with lime in open pans, and to decompose the insoluble lime salt of the fatty acids with sulphuric acid. This was superseded by the action of steam alone under pressure, or of superheated steam. Saponification is now usually effected by strong sulphuric acid in the case of the poorer qualities of fat, which are much discoloured and have a strong smell (p. 282). Purer fats are hydrolysed by the action of superheated steam in closed boilers, or autoclaves, under

pressure, with the addition of about 2 per cent. of lime to the fat used. The following equation expresses the reaction in the case of stearin—

$$\begin{array}{l} C_{17}H_{35}CO{\cdot}OCH_2 + H{\cdot}OH \\ \qquad\qquad\quad | \\ C_{17}H_{35}CO{\cdot}OCH \;\, + H{\cdot}OH = \underset{\text{Stearic acid.}}{3C_{17}H_{35}CO{\cdot}OH} + \underset{\text{Glycerol.}}{C_3H_5(OH)_3}. \\ \qquad\qquad\quad | \\ C_{17}H_{35}CO{\cdot}OCH_2 + H{\cdot}OH \\ \qquad\quad \text{Stearin.} \end{array}$$

After saponification, the "sweet water," which contains the glycerol, is drawn off, a little sulphuric acid is added to decompose the lime salts, and the fatty acids, which float on the surface, are removed, and may be purified by distillation with superheated steam. The acids are pressed hot to remove the liquid oleic acid and a firmer cake is thereby produced. The cake is melted with the addition of a little paraffin wax, and moulded into candles.

Soap Manufacture.—The term saponification was originally applied to the manufacture of soap. **Hard soap** is the sodium salt, **soft soap**, the potassium salt, of the acids of fat. Consequently, caustic soda and caustic potash are always used for the saponification of the fat in soap-making. The reaction which takes place may be illustrated in the case of stearin—

$$\underset{\text{Stearin.}}{(C_{17}H_{35}COO)_3C_3H_5} + 3NaOH = \underset{\text{Sodium stearate.}}{3C_{17}H_{35}COONa} + \underset{\text{Glycerol.}}{C_3H_5(OH)_3}.$$

EXPT. 56.—Thirty grams of tallow are placed in a beaker and melted by steam passed in from a flask (with safety tube) containing boiling water. After a short interval, 60 c.c. of a 10 per cent. solution of caustic soda are added and steam driven through until a clear brown solution is obtained. The soap is then separated by the addition of salt. An alcoholic solution of caustic potash or soda for saponifying oils and fats is much more rapid in its action than an aqueous one, which does not dissolve the fat. Make a ten per cent. solution of caustic soda in methyl alcohol. Place a little lard in a porcelain basin on the water-bath, cover it with the alcoholic soda solution, and stir. When the fat has dissolved, heat for a few minutes to remove the alcohol. A hard mass will remain. It is the sodium salts of the fatty acids mixed with glycerol. It readily dissolves in water, especially on warming. Divide the solution into two portions. To one add dilute hydrochloric acid, when a thick curdy precipitate of the fatty acids separates, which on heating melts and floats on the surface; on cooling, it becomes a

solid cake. To the other portion add strong sodium chloride solution, when a precipitate of the sodium salts of the fatty acids is formed.

The manufacture of soap is carried on in large iron pans, which are heated by steam pipes. Fat, which has been previously "rendered," or melted and strained from cellular tissue, or a mixture of fat and oil, is used. Beef and mutton tallow and olive oil make the best hard, or curd soap. For cheaper soaps, palm oil, palm-nut, cocoa-nut, cotton-seed, and various other vegetable oils, together with rosin (which contains an acid, and forms a sodium salt), and oleic acid from the candle industry, are employed. The fat and oil are mixed with caustic soda solution, or "lye," and boiled until hydrolysis is complete, and the materials have become converted into the sodium salts of the fatty acids. Salt is now added, which causes the sodium salts, or soap, to separate as a white granular mass on the surface. The lower aqueous layer or "spent lyes," containing the glycerol, is drawn off and used for the production of glycerol. The soap is again heated with the addition of a little caustic soda to ensure complete saponification, and the hot, pasty mass, after being allowed to settle two or three days, is run or pumped into frames to cool and set.

In the *cold process* a strong solution of caustic soda is mixed with cocoa-nut oil and tallow. Saponification occurs with rise of temperature, and the mass sets to a hard soap.

A new and interesting commercial method of saponification is the *Twitchell process*, in which a compound of benzene- or naphthalene-sulphonic acid with stearic or hydroxystearic acid is used as the hydrolytic agent, and acts as a catalyst. Saponification of oils and fats may also be effected by the enzyme, *lipase*, which occurs in certain seeds, especially castor oil seed, and in certain animal organs (pancreas, liver). A very small amount has the property of rapidly hydrolysing large quantities of fats and oils at the ordinary temperature. In this way the free fatty acids are obtained, which combine to form soap with sodium carbonate, thus dispensing with the more expensive caustic alkali.

Analysis of Soap.—The quality of soap is determined by estimating the amount of water, fatty acid, and alkali present The amount of water is estimated by heating a weighed quantity of soap gradually to 100°–110° until the weight is constant. The

quantity of fatty acid and alkali are determined by dissolving a weighed amount of the soap in water, adding excess of standard hydrochloric or sulphuric acid, and heating until the melted fatty acids form a liquid layer on the surface. The fatty acids, on cooling, set, as a rule, to a hard cake, which is removed, dried, and weighed. If the acids remain liquid, a weighed amount of paraffin or beeswax is added, which is melted with the fatty acids, and gives the necessary consistency to the mass on cooling. The quantity of alkali is found by adding standard alkali to the solution, from which the fatty acids have been removed, until neutrality is reached. The difference between the amount of acid taken and the alkali used, gives the quantity of alkali in the soap. Free alkali in a toilet soap is very objectionable, and its amount is estimated by dissolving the soap in alcohol, and adding a drop or two of phenolphthalein solution as indicator. The presence of free alkali produces a red colour, and the amount may be estimated by adding standard acid until the red colour disappears.

Varieties of Soap.—*White curd soap* is made from tallow; the different kinds of *yellow soap* usually contain some rosin; *Castile soap* consists largely of sodium oleate, and is made from olive oil; *marine soap* is prepared from cocoa-nut oil, and dissolves in salt water; *transparent soap* is made by dissolving ordinary yellow soap in methylated spirit, and, after driving off the alcohol, pouring out the liquid, which, on cooling, forms a transparent mass; *soft soap* is made by saponifying oil, or fat, with caustic potash. The product forms a dark-coloured emulsion, which contains excess of alkali and all the glycerol of the original materials; *lead soap*, or lead plaster, is prepared by boiling olive oil with litharge. Some so-called soaps, which are used for cleaning rather than for washing in the ordinary sense, consist chiefly of fine sand, pipe-clay, or fuller's earth, and little real soap. *Dry soap* is made by drying ordinary soap and grinding it with a certain amount of sodium carbonate.

The variety of materials used in the manufacture of soap is so great that the mere proportion of water, alkali, and acid gives no very definite information as to the real value of a soap. Good curd soap for household purposes contains no free alkali, and not more than 30 per cent. of water, which must be regarded as combined water. "Toilet"

or "milled" soap, made from compressed shavings of partially dried soap, generally contains much less water. On the other hand, cheap soaps made from cocoa-nut oil, etc., may contain as much as 80 per cent. of water.

THE DETERGENT ACTION of soap appears to be a purely physical phenomenon, depending partly on surface tension, *i.e.* the internal attraction of the molecules for those lying near the surface of a liquid, the effect being to contract the surface as much as possible, giving rise to the spheroidal condition, *e.g.* drops of water in air or suspended oil drops in water. Soap acts in a variety of ways. It causes the surface of the grease particles to be wetted by lowering the surface tension between the soap and grease particles. The lowering of the tension may be shown by allowing drops of oil to pass from the end of a pipette bent in the form of a hook, first into water and then into a soap solution. In the first case the drops escape in the spheroidal form: but in the second case the oil is drawn out into a thin cylindrical shape. The effect is best shown with the aid of a lantern and screen. The soap forms a skin round the particles and so promotes emulsification. The process of emulsification of the grease liberates the dirt particles, which are prevented from adhering to the greasy material by their rapid oscillations (Brownian movement) and from coalescing by the negative charge they receive due to the presence of alkali. They are thus removed in a fine state of division along with the greasy matter with which they were originally surrounded.

Wool-grease, or *Yorkshire grease*, is obtained from the scourings of wool, and contains, in addition to fatty acids, the alcohol *cholesterol*, $C_{27}H_{46}O$. It is commonly separated from the washings by "cracking" or adding sulphuric acid, which causes the greasy matter to rise to the surface, and it is then skimmed off. A more complete separation is effected by concentrating the wash liquors, and then separating the grease by means of a centrifugal extractor. The grease, which is specifically lighter, passes to the centre of the rotating cylinder, whence it flows away. It forms a brown semi-solid mass, which gives a colourless emulsion with water, and is used as an ointment, known as *lanoline*.

Butter.—Good cows' butter contains on the average about 90 per cent. of fat, 1 per cent. of curd, 1 per cent. of salt, and 8 per cent. of water. Butter fat consists mainly of stearin, palmitin, and olein, with about 7 per cent. of butyrin, and 2 per cent. of caproin, caprylin, and caprin. The purity of a butter may be roughly determined by saponifying a weighed sample with caustic

soda, acidifying with sulphuric acid, and distilling. The volatile fatty acids collect in the distillate and are estimated by titration with alkali. The quantity of water is determined by drying the sample in a steam oven; the amount of salt and curd, by melting, filtering on a weighed filter, and washing the filter with ether until free from fat. The curd and salt remain, and the salt is then estimated by igniting the filter paper and burning off the organic matter.

Butter Substitutes, Margarine.—Beef tallow or suet is heated to a temperature of 35° and subjected to pressure. The lower melting portion, which is expressed, contains a large quantity of olein, and when mixed with certain vegetable oils (cotton seed, sesame, arachis, cocoa-nut, or other nut oils), and occasionally a little milk and genuine butter, constitutes margarine. The quantity of volatile fatty acid (butyric acid) present as butyrin is always considerably below that in genuine butter. Nevertheless, margarine, if properly prepared, is a perfectly wholesome article of diet.

Expt. 57.—The difference between butter and margarine may be shown on a small scale by adding to a small quantity of each in a test-tube a few c.c. of a methyl alcohol solution of caustic soda and boiling until most of the alcohol is driven off. On cooling and adding dilute hydrochloric acid, the unpleasant smell of butyric acid is given by the butter, but is scarcely noticeable in the case of margarine.

The Hardening of Fats and Oils.—The chief difference between a soft fat or oil and a hard fat is the greater proportion of oleate which it contains. Now, oleic acid contains two fewer hydrogen atoms in the molecule than stearic acid, to which it can be reduced by the action of hydrogen in the presence of a suitable catalyst. In 1899 Sabatier and Senderens found that finely divided nickel was the most effective catalyst for the purpose, and to-day the process is worked on the large scale. The hydrogen is obtained electrolytically, and the purified nickel is suspended in the liquid, which is heated to 140°–180° C. In this way triolein (p. 280) is converted to tristearin.

Questions on Chapter X

1. Describe a method for separating the constituents of a mixture consisting of methyl alcohol, acetone, and acetic acid.

2. By what series of reactions can ethyl alcohol be converted into propionic acid?

3. Discuss the structural formula of acetic acid.

4. Describe the reactions by which fatty acids may be converted into paraffins, aldehydes, and ketones.

5. How would you obtain a specimen of pure acetic acid from vinegar?

6. Define "hydrolysis," and give examples. Name the different ways in which fat may be hydrolysed.

7. Describe briefly the manufacture of soap. How are the water, fatty acid, and alkali estimated in soap?

8. What are the general characters of oils, fats, and waxes?

9. What is the composition of butter and margarine? How can they be distinguished?

10. Give a list of methods for preparing the fatty acids.

11. Describe the "quick vinegar" process.

12. Give the formula for the *acyl* group in the first six members of the fatty acids.

13. Explain the action of glycerol in the preparation of formic acid.

14. Account for the action of formic acid on silver nitrate. How is formic acid distinguished from acetic acid? In what respects do these acids resemble one another?

15. Write precise instructions for the preparation of sodium formate, using oxalic acid as the source.

16. How would you detect formic acid in acetic acid?

17. Starting from methyl alcohol, explain, illustrating your answer by equations, how acetic acid can be produced. How can acetic acid be reconverted into methyl alcohol?

18. The ratio of carbon, hydrogen, and oxygen in acetic acid can be expressed by the formula CH_2O. What are the reasons that have led to the formulæ $C_2H_4O_2$ and $CH_3{\cdot}COOH$ being used instead?

19. You are given the product of the distillation of wood. Describe how a specimen of pure acetic acid could be obtained from it.

20. How has the constitution of the glycerides been determined? State the constitution and the chief constituents of the more important natural fats.

CHAPTER XI

THE ACID CHLORIDES, THE ANHYDRIDES, AND THE AMIDES

The Acid or Acyl Chlorides are prepared by the action of phosphorus trichloride or pentachloride on the fatty acids. Acetic acid and phosphorus trichloride give acetyl chloride and phosphorous acid; when the pentachloride is used, phosphorus oxychloride and hydrochloric acid are formed—

$$3CH_3{\cdot}CO{\cdot}OH + PCl_3 = \underset{\text{Acetyl chloride.}}{3CH_3{\cdot}CO{\cdot}Cl} + P(OH)_3.$$

$$CH_3{\cdot}CO{\cdot}OH + PCl_5 = CH_3{\cdot}CO{\cdot}Cl + HCl + POCl_3.$$

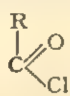
A more convenient reagent is thionyl chloride, the by-products of which escape as gases.

$$CH_3{\cdot}CO{\cdot}OH + SOCl_2 = CH_3{\cdot}CO{\cdot}Cl + SO_2 + HCl.$$

Formyl chloride, $H{\cdot}CO{\cdot}Cl$, is unknown. It probably decomposes at once into carbon monoxide and hydrochloric acid.

Expt. 58. *Preparation of Acetyl Chloride.*—A distilling flask, through the neck of which a tap-funnel is inserted, is attached to a condenser and receiver. The receiver should be connected with a tower of soda-lime, to absorb the hydrochloric acid evolved; otherwise, the operation must be conducted in a fume-cupboard. Fifty grams of glacial acetic acid are placed in the flask, and 40 grams of phosphorus trichloride are slowly added from the tap-funnel. The flask is gently warmed in the water-bath to 40°–50°, until the evolution of hydrochloric acid gas slackens. The water-bath is then heated to boiling, when the acetyl chloride distils. It boils at 55°.

These compounds are denoted as chlorides of the acid radicals, or as acid or acyl chlorides. Their structure represents them as substitution products of the aldehydes, and they yield aldehydes on reduction (p. 177). Their general formula is



Properties of Acid Chlorides.—The acid chlorides are colourless liquids or solids with boiling-points lying between those of the corresponding aldehyde and acid. They fume in moist air, and are very quickly decomposed by water. Hydrochloric acid is thereby evolved, and the original acid regenerated. Acetyl chloride, when acted on by water, gives acetic acid—

$$CH_3{\cdot}CO\boxed{Cl + H}OH = CH_3{\cdot}CO{\cdot}OH + HCl.$$

EXPT. 59.—Add a few drops of water to a few drops of acetyl chloride in a test-tube. Decomposition takes place rapidly and the liquid becomes hot.

The action of the alcohols on the acid chlorides is very similar to that of water. The alkyl salts, or esters, are formed and hydrochloric acid is evolved. Acetyl chloride and ethyl alcohol in this way give ethyl acetate—

$$CH_3{\cdot}CO\boxed{Cl + H}OC_2H_5 = \underset{\text{Ethyl acetate.}}{CH_3{\cdot}CO{\cdot}OC_2H_5} + HCl.$$

This reaction is of great importance as a means of detecting the presence of a hydroxyl group in organic substances, and is more convenient than that requiring the use of sodium or of phosphorus pentachloride (p. 97), as the acetyl derivatives which are formed are usually easy to purify. Acetyl chloride, being readily obtainable, is the most convenient acid chloride to employ. In compounds in which the hydroxyl group occurs, the hydrogen is replaced by *acetyl*, and forms an *acetoxyl group*—

$$—OH + CH_3COCl = \underset{\text{Acetoxyl.}}{—O{\cdot}CO{\cdot}CH_3} + HCl.$$

EXPT. 60.—To about 1 c.c. of ethyl alcohol in a test-tube add, drop by drop, 1 c.c. of acetyl chloride and cool well under the tap. Then add about 1 c.c. of a solution of common salt, in which ethyl acetate is only slightly soluble. Ethyl acetate separates out on the surface of the liquid, and may be recognised by its fragrant smell.

Ammonia and the amines (p. 200) react with acid chlorides, forming compounds known as *amides* (p. 178). Acetyl chloride

and ammonia yield acetamide. If excess of ammonia is used, ammonium chloride is formed as well—

$$CH_3{\cdot}CO{\cdot}\boxed{Cl + H}NH_2 + NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + NH_4Cl.$$

Ammonia. Acetamide.

EXPT. 61.—If ammonia solution is added to acetyl chloride, heat is evolved; but the acetamide, being very soluble in water, does not separate. If, however, a substituted ammonia, or amine, like phenylamine (aniline), $NH_2{\cdot}C_6H_5$, be taken, the solid phenyl acetamide (acetanilide), $CH_3{\cdot}CO{\cdot}NHC_6H_5$, separates out. The experiment may be performed with a drop or two of each substance.

The acid chlorides on reduction in presence of palladium and hydrogen yield aldehydes (p. 129).

The Anhydrides are obtained by the action of the acid chloride on the sodium salt of the corresponding acid. Acetyl chloride and sodium acetate yield acetic anhydride.

$$CH_3{\cdot}CO{\cdot}\boxed{Cl + Na}O{\cdot}CO{\cdot}CH_3 = CH_3{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 + NaCl.$$

Acetic anhydride.

The reaction is similar to that by which ethers are prepared (p. 119), and as the ethers are also named alkyl oxides, these compounds may be regarded as *acyl oxides*. By taking the chloride of one acid and the sodium salt of another, *mixed anhydrides* are formed, a process which resembles the method of preparing mixed ethers (p. 121)—

$$O\begin{cases} CH_3. \\ CH_3. \end{cases} \qquad O\begin{cases} CO{\cdot}CH_3. \\ CO{\cdot}CH_3. \end{cases}$$

Alkyl oxide. Acyl oxide.

EXPT. 62. *Preparation of Acetic Anhydride.*—A retort, through the tubulure of which a tap-funnel is fixed, is attached to a condenser and receiver. Fifty-five grams of fused sodium acetate are placed in the retort, and 40 grams of acetyl chloride are slowly run in from the tap-funnel, the retort being cooled in water. When the acetyl chloride has been added, the contents of the retort are well stirred with a glass rod and then distilled. Acetic anhydride distils at 130°–140°.

The anhydrides possess a pungent smell, but do not fume. They have a higher boiling-point than the acids from which they are derived. They closely resemble the acid chlorides in chemical behaviour, being decomposed by water, alcohol, and ammonia.

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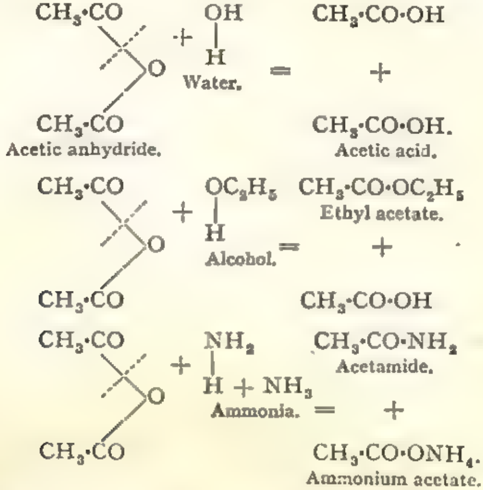
but much less rapidly than the acid chlorides. Acetic anhydride yields the same products as acetyl chloride with these three reagents—



The Amides are formed by the action of ammonia on acid chlorides (p. 176), on the anhydrides (see above), and on the esters (p. 187). They may be prepared by the *partial* hydrolysis of the alkyl cyanides with moderately strong sulphuric acid. Complete hydrolysis converts the cyanide into the acid. Methyl cyanide first forms acetamide and then acetic acid and ammonia. The two reactions may be represented as follows :—

1. $CH_3{\cdot}CN + H_2O = \underset{\text{Acetamide.}}{CH_3{\cdot}CO{\cdot}NH_2}.$

2. $CH_3{\cdot}CO{\cdot}NH_2 + H_2O = \underset{\text{Ammonium acetate.}}{CH_3{\cdot}CO{\cdot}ONH_4}.$

One of the most convenient methods for obtaining the amides is to heat or distil the ammonium salt of the acid. The salt loses one molecule of water in the process. Ammonium acetate gives acetamide—

$$\underset{\text{Ammonium acetate.}}{CH_3{\cdot}CO{\cdot}ONH_4} = \underset{\text{Acetamide.}}{CH_3{\cdot}CO{\cdot}NH_2} + H_2O.$$

All these reactions indicate that amides are derivatives of the acids, in which the hydroxyl is replaced by an **amido** group (NH_2).

EXPT. 63. *Preparation of Acetamide.*—Melt 50 grams of ammonium acetate by gently heating the salt and pour the liquid into a distilling flask (200 c.c.) with the side-tube plugged with a short piece of rubber tube and glass rod. Add 60 c.c. glacial acetic acid and boil gently with reflux condenser for four hours. The product is distilled as follows: insert a thermometer into the neck of the flask and use a long, wide tube as a condenser (Fig. 64). Heat the flask over wire gauze. A certain quantity of acetic acid and water distils. When the temperature reaches 210°, change the receiver; the distillate on cooling solidifies as a mass of colourless crystals consisting mainly of acetamide. Acetamide melts at 82° and boils at 222°. The smell, which resembles that of mice, proceeds from a minute trace of impurity.

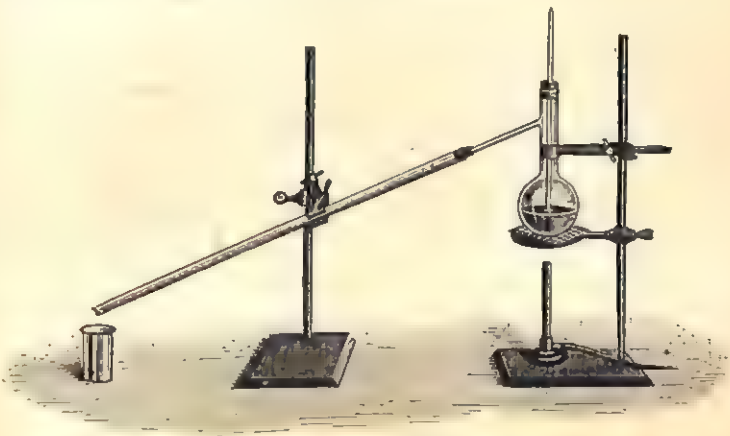


FIG. 64.—Preparation of Acetamide.

Properties of the Amides.—The amides, with the exception of *formamide*, $HCO{\cdot}NH_2$, which is liquid at the ordinary temperature, are colourless, crystalline solids with high boiling-points. Formamide boils at 212°, acetamide at 222°, propionamide at 213°, etc.

The lower members are very soluble in water, and the solution is neutral to litmus. They form loose combinations with hydrochloric acid when the gas is passed into a solution of the amide in ether; but the compounds are quickly decomposed by water.

By the action of dehydrating agents (*e.g.* phosphorus pentoxide) the amides are converted into alkyl cyanides. Acetamide, when

mixed with phosphorus pentoxide and distilled, gives methyl cyanide—

$$\underset{\text{Acetamide.}}{CH_3\cdot CO\cdot NH_2} - H_2O = \underset{\text{Methyl cyanide.}}{CH_3CN.}$$

When boiled with caustic alkalis, strong hydrochloric acid, or moderately strong sulphuric acid, the amides are hydrolysed and form a fatty acid and ammonia. Acetamide is converted into acetic acid and ammonia—

$$CH\ \cdot CO\cdot NH_2 + H_2O = CH_3\cdot COOH + NH_3.$$

EXPT. 64.—Boil a small quantity of acetamide with caustic soda solution in a test-tube, and smell the vapour given off, or test it with red litmus. Ammonia is evolved, and sodium acetate is found in solution—

$$CH_3\cdot CO\cdot NH_2 + NaOH = CH_3\cdot CO\cdot ONa + NH_3.$$

Thus, the three classes of compounds, the ammonium salts of the acids, the amides, and cyanides, are intimately related and may be converted one into the other. Ammonium acetate, on distillation, yields acetamide; when distilled with a large quantity of phosphorus pentoxide, it may be directly converted into methyl cyanide. Acetamide, when distilled with phosphorus pentoxide, forms methyl cyanide, whilst, on hydrolysis, it is converted into acetic acid and ammonia. Methyl cyanide gives acetamide by partial hydrolysis, and acetic acid and ammonia when the process is carried to completion. These changes are indicated in the following diagram:—

$$\begin{tikzcd} \underset{\text{Ammonium acetate}}{CH_3\cdot CO\cdot ONH_4} \arrow[rr, shift right] \arrow[dr, shift left] & & \underset{\text{Acetamide.}}{CH_3\cdot CO\cdot NH_2.} \arrow[ll, shift right] \arrow[dl, shift left] \\ & \underset{\text{Methyl cyanide.}}{CH_3\cdot CN.} \arrow[ul, shift left] \arrow[ur, shift left] & \end{tikzcd}$$

Some of the brominated amides such as *neuronal*,

$$(C_2H_5)_2CBr\cdot CONH_2,$$

are used as hypnotics.

Questions on Chapter XI

1. Describe the preparation of acetyl chloride.

2. In what manner can an acid chloride be employed to indicate the presence of a hydroxyl group in an organic compound? Illustrate this by reference to propyl alcohol. What advantage has this reagent over phosphorus chloride or sodium?

3. Describe by means of equations the behaviour of propionyl chloride with the following reagents: water, methyl alcohol, ammonia, palladium and hydrogen, sodium propionate.

4. Compare the behaviour of alkyl and acyl oxides with different reagents.

5. Describe two methods for the preparation of acetamide.

6. Explain the various stages in the process by which (1) acetic acid is converted into methyl cyanide, and (2) methyl cyanide into acetic acid.

7. Describe the method and apparatus you would employ for the preparation of acetyl chloride. How is it acted upon by each of the following substances: (1) sodium hydrate, (2) ethyl alcohol, (3) ammonia? Give equations.

8. Describe the materials required and all the operations involved in making acetic anhydride.

9. Starting with acetyl chloride, show how acetamide, acetic acid, and acetic anhydride respectively may be obtained from it.

10. Describe two methods for the preparation of acetamide. How would you convert it into (1) acetic acid, (2) methylamine?

CHAPTER XII

THE ESTERS

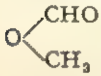
Esters are formed by the action of an alcohol on an organic or inorganic acid, just as salts are produced by the action of a base on an acid (p. 97).

Methyl alcohol and formic acid, for example, give methyl formate, just as caustic soda and formic acid yield sodium formate—

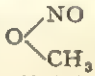
$$HCO\cdot OH + H\cdot OCH_3 = \underset{\text{Methyl formate.}}{HCO\cdot OCH_3} + H_2O.$$

$$HCO\cdot OH + H\cdot ONa = \underset{\text{Sodium formate.}}{H\cdot CO\cdot ONa} + H_2O.$$

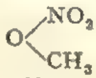
The following are the formulæ of a series of alkyl esters :—



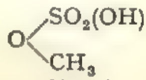
Methyl formate.



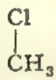
Methyl nitrite.



Methyl nitrate.



Methyl hydrogen sulphate.



Methyl chloride.

With the exception of the halide esters like methyl chloride, the alkyl group in the ester is united by oxygen to the acid radical.

Esters of Organic Acids.—The esters of the fatty acids, which we shall consider first, were studied in 1782 by Scheele, who discovered a method for their preparation which, with a little modification, is still in general use.

Sources of the Esters.—The esters form the sweet-smelling constituents, or *ethereal oils*, of many plants, and on account of their fragrant smell they are manufactured as a substitute for natural perfumes and fruit essences. They may be prepared by the action of an alcohol on an acid chloride or anhydride (pp. 176, 178), or by heating the silver salt of the acid with an alkyl iodide dissolved in ether. Silver acetate and ethyl iodide yield ethyl acetate—

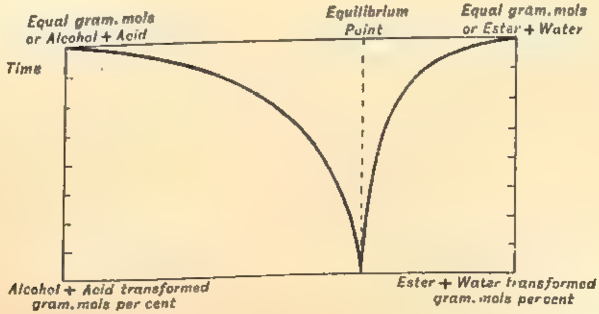
$$CH_3\cdot COOAg + IC_2H_5 = CH_3\cdot COOC_2H_5 + AgI.$$

Reversible or Balanced Reactions.—The most common method for preparing esters is to heat together the acid and the alcohol. The reaction is, however, a reversible one (p. 101). A condition of equilibrium is attained when a certain ratio exists between the

amount of ester and water and that of free acid and alcohol. The point of equilibrium varies with the conditions of the experiment, namely, the nature and relative quantity of the alcohol and acid and the temperature. Berthollet (1799) was the first to draw attention to the effect of quantity. He showed that the amount of chemical change c is proportional to the product of the quantity of the reacting substances a and b and their affinity K. This is known as *the law of mass action* and is represented by the equation :

$$c = K \times ab.$$

The only change introduced since Berthollet's time is in the meaning of a and b, which now stand for molecular proportions and not actual weights. Guldberg and Waage (1867) showed that K can be determined by studying the conditions of equilibrium in the following way. Suppose a curve is drawn of the action of an equal number of gram-molecules of ethyl alcohol and acetic acid, the quantity transformed into ester and water being plotted on the horizontal, and the time on the vertical. This can be done by keeping the mixture in a thermostat and removing a little from time to time, and titrating the amount of free acid present. It will be found that, as the quantity of acid and alcohol diminishes, the velocity (quantity in equal times) also diminishes until there is no further change. This is the equilibrium point. If the reaction is begun from the other end and a mixture of an equal number of gram-molecules of ester and water is taken, free acid will make its appearance, and the reaction will quickly slow down until the same equilibrium point is reached. The following curves will be obtained :—



The equilibrium point is reached when two-thirds of a gram-molecule of ester and water and one-third of a gram-molecule of acid and alcohol are present. The reaction may be represented by the following equation :—

$$\underset{\frac{1}{3}}{C_2H_5OH} + \underset{\frac{1}{3}}{CH_3{\cdot}COOH} \rightleftarrows \underset{\frac{2}{3}}{CH_3{\cdot}COOC_2H_5} + \underset{\frac{2}{3}}{H_2O}.$$

We may consider the subject in another way and suppose that equilibrium is reached when the number of molecules of acid and alcohol formed in unit time are exactly equal to the number of molecules of ester and water decomposed, or, in other words, when the velocities of the opposing reactions are equal, that is, when

$$V_1 = V_2.$$

According to the kinetic theory the velocity of a reaction is determined by the number of collisions between molecules; but the number of collisions in unit time is proportional to the number of molecules in unit volume (concentration). For let us take the following three cases, and let us suppose that in the first case there is one molecule of alcohol and one molecule of acid in unit volume and one collision in unit time. Now double the number of each kind of molecule; it is clear that, without any change in their rate of movement, each molecule has only half the distance to travel before meeting another molecule and therefore hits two in unit time. As each has two encounters there will be 4 (2×2) collisions. In the same way, if the number is doubled again each molecule will hit 4 in unit time, and there will be 16 (4×4) collisions. Therefore the velocity of a reaction is proportional to the product (not the sum) of the reacting molecules in unit volume.

Let a and b = number of molecules of reacting substances in unit volume (concentration) and c and d = number of molecules of products in unit volume (concentration). The velocities of the two reactions will be :

$$V_1 = K_1ab, \text{ and } V_2 = K_2cd.$$

When there is equilibrium, $V_1 = V_2$,

and
$$K_1ab = K_2cd,$$

or
$$\frac{K_1}{K_2} = \frac{cd}{ab}, \text{ replacing } \frac{K_1}{K_2} \text{ by } K$$

$$K = \frac{cd}{ab}.$$

In the above example,

$$K = \frac{c_{\text{ester}} \times d_{\text{water}}}{a_{\text{alcohol}} \times b_{\text{acid}}} = \frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = 4.$$

K, which is here represented by the number 4, is called the *equilibrium constant*. It may be used for determining the amount of ester produced for any known mixture of ethyl alcohol and acetic acid at the same temperature.

If $x =$ required gram-mols. of ester (= water)
$1 =$ concentration (gram-mols.) of alcohol
$m =$ " " acid

then
$$\frac{x^2}{(1-x)(m-x)} = 4,$$

from which x can be determined.

Fischer and Speier found that the addition to the alcohol of about 3 per cent. of hydrochloric acid gas, or the same quantity of concentrated sulphuric acid, enables the reaction to be completed on heating.

EXPT. 65. *Preparation of Ethyl Acetate.*—METHOD 1. Bubble hydrochloric acid gas through 25 c.c. of ethyl alcohol cooled in water, until the alcohol has absorbed 4–5 grams. Mix the alcohol with an equal volume of acetic acid, and boil the mixture in a flask (attached to an inverted condenser, the top of which is connected to a soda-lime tower to absorb the acid fumes) on the water-bath for half an hour. Pour the liquid into strong brine. The ethyl acetate separates as a layer on the surface, and may be removed by means of a separating-funnel. The liquid is then dehydrated with solid calcium chloride and distilled from the water-bath. It boils at 77°–78°.

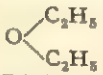
METHOD 2. Mix together equal volumes of concentrated sulphuric acid and ethyl alcohol, and heat the mixture in a paraffin bath to 140°, using the form of apparatus shown in Fig. 55, p. 119. Drop in from the tap-funnel a mixture of equal volumes of glacial acetic acid and ethyl alcohol at the same speed as that at which the liquid distils. The distillate contains the ester and also some acetic acid, alcohol ether, sulphurous acid, and water. The distillate is shaken with a strong solution of sodium carbonate, which is then drawn off and replaced by strong brine. The brine, on shaking, dissolves the alcohol, and is then separated from the ester, which is finally dehydrated over solid calcium chloride, and distilled.

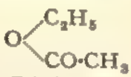
A good yield is also obtained by using much less sulphuric acid, the presence of which is apt to cause decomposition.

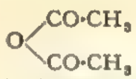
A modern industrial process has been successfully operated in which ethyl acetate is produced by the polymerisation of acetaldehyde (from acetylene) (p. 264), in the presence of anhydrous aluminium chloride and ethyl alcohol.

$$2CH_3{\cdot}CH{:}O = CH_3{\cdot}COOC_2H_5$$

Properties of the Esters.—The esters are neutral and colourless substances with a fragrant smell, and are for the most part liquids which do not mix with water. The methyl and ethyl esters have lower boiling-points than the acids from which they are prepared. The esters in point of structure occupy an intermediate position between the ethers and anhydrides—

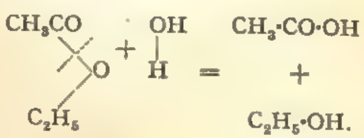

Ethyl ether.


Ethyl acetate.


Acetic anhydride.

Their relation to the ethers has given rise to the expression *compound ethers*, and to names such as *acetic ether*, by which the esters were at one time known.

In chemical behaviour the esters stand midway between the very stable ethers and unstable anhydrides. The esters are slowly decomposed by water; much more rapidly by caustic alkalis in aqueous solution; still more rapidly by alkalis in alcoholic solution. The process is one of *hydrolysis*. The elements of water are taken up, and the ester is converted into acid and alcohol. Ethyl acetate gives alcohol and acetic acid—



The reaction is, in fact, identical with the saponification of fats and oils (p. 168), the alcohol in the latter case being glycerol.

EXPT. 66. *Hydrolysis of Ethyl Acetate.*—Heat 20 grams of ethyl acetate with three times its volume of aqueous potash solution of about 30 per cent. strength. The mixture is placed in a distilling flask, attached by the neck to an inverted condenser, and boiled over wire-gauze. A piece of porous pot is placed in the flask to prevent bumping,

and the side-tube of the distilling flask is temporarily closed with a stopper. When the layer of ethyl acetate has dissolved (the potassium acetate and ethyl alcohol being both soluble in water), the condenser is attached to the side-tube of the distilling flask and the liquid distilled. The alcohol which passes over may be separated from the water by the addition of potassium carbonate, which causes the alcohol to float on the surface, and it may then be withdrawn. The acetic acid remains in the distilling flask, as the potassium salt. The alkali is carefully neutralised with sulphuric acid and the liquid evaporated to dryness. The dry residue is then distilled with strong sulphuric acid, when pure acetic acid passes over. The reaction is expressed by the following equation—

$$\underset{\text{Ethyl acetate.}}{CH_3{\cdot}CO{\cdot}OC_2H_5} + KOH = \underset{\text{Potassium acetate.}}{CH_3{\cdot}CO{\cdot}OK} + \underset{\text{Alcohol.}}{C_2H_5{\cdot}OH.}$$

The action of ammonia on the esters is rather different from that of caustic potash or soda; in this case alcohol is formed, but the ammonia remains attached to the acid radical, forming an amide (p. 178). Ethyl acetate gives acetamide and ethyl alcohol—

$$\begin{array}{l} CH_3{\cdot}CO \\ \quad\;\; \diagdown \\ \qquad\; O \\ \quad\;\; \diagup \\ C_2H_5 \end{array} + \begin{array}{c} NH_2 \\ | \\ H \end{array} = \underset{\text{Acetamide.}}{CH_3{\cdot}CO{\cdot}NH_2} + \underset{\text{Alcohol.}}{C_2H_5OH}$$

Expt. 67.—The action of ammonia on ethyl acetate cannot be used to demonstrate this change, as the resulting acetamide is too soluble to separate. If, however, ethyl oxalate is employed, the insoluble oxamide is at once precipitated on adding strong ammonia—

$$\underset{\text{Ethyl oxalate.}}{\begin{array}{l} CO{\cdot}OC_2H_5 \\ | \\ CO{\cdot}OC_2H_5 \end{array}} + \begin{array}{c} NH_3 \\ \\ NH_3 \end{array} = \underset{\text{Oxamide.}}{\begin{array}{l} CO{\cdot}NH_2 \\ | \\ CO{\cdot}NH_2 \end{array}} + 2C_2H_5OH.$$

Isomerism of the Esters.—The general formula of the esters of the fatty acids is $C_nH_{2n}O_2$, *i.e.* the same as that of the fatty acids. The esters are readily distinguished from the acids by their neutral reaction, and, in the case of the lower members, by their smell and insolubility in water. Moreover, the esters, unlike the fatty acids, are insoluble in dilute solutions of the alkalis. Among the esters themselves, isomerism may arise from the presence of isomeric acids or alcohols forming the constituent parts of the ester. Examples of this kind of isomerism are ethyl butyrate and ethyl isobutyrate, and propyl and isopropyl acetate. Finally, isomerism may be

produced by the union of acids and alcohols to form esters, in which both constituents differ in the different isomers. A compound of the formula $C_4H_8O_2$ may represent methyl propionate, ethyl acetate, or propyl formate—

$C_2H_5CO{\cdot}OCH_3$, Methyl propionate.
$CH_3{\cdot}CO{\cdot}OC_2H_5$, Ethyl acetate.
$H{\cdot}CO{\cdot}OC_3H_7$, Propyl formate.

Such compounds may be readily distinguished by hydrolysis followed by the separation of the alcohol and acid, according to the method described in Expt. 66, p. 186. The alcohol is identified by its boiling-point or other distinctive property; the acid is tested for in the residue left after removal of the alcohol.

Artificial Essences.—It has already been stated that the esters are manufactured as substitutes for natural essences. The following compounds are commonly used for this purpose: ethyl formate (rum), isoamyl acetate (pear), ethyl butyrate (pine-apple), isoamyl isovalerate (apple).

The student is reminded that the constituents of butter (p. 172), fats, oils, (p. 166), beeswax, Chinese wax, and spermaceti (p. 116), belong to the group of esters.

Ethyl Acetoacetate.—If a small piece of sodium is added to ethyl acetate, a gradual effervescence begins, which gains in force as the action proceeds. The sodium dissolves and hydrogen is evolved. The reaction was discovered by Geuther (1863), and was further investigated by Frankland and Duppa (1865). The product of the reaction is the sodium compound of ethyl acetoacetate, from which the free ester may be separated by the addition of acetic acid followed by the fractional distillation of the oil which separates. Acetoacetic ester is a colourless liquid with a fruity smell. It has the formula—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}OC_2H_5.$$
Ethyl acetoacetate.

This formula represents ethyl acetate in which one hydrogen atom of the methyl group is replaced by the acetyl group $CH_3{\cdot}CO$. The properties of this important substance will be discussed in a subsequent chapter (p. 328).

Esters of Inorganic Acids.—These esters are prepared by similar methods to those used in the preparation of the esters of organic acids. The action of the alcohol on the acid chloride may be illustrated in the case of dimethyl sulphite, which is prepared from thionyl chloride, $SOCl_2$, and methyl alcohol—

$$\underset{\text{Thionyl chloride.}}{SOCl_2} + 2CH_3OH = \underset{\text{Dimethyl sulphite.}}{SO(OCH_3)_2} + 2HCl.$$

Dimethyl Sulphate is conveniently prepared by dropping methyl alcohol into well cooled chlorosulphonic acid. The mixture is then distilled under reduced pressure, which converts the methyl sulphuric acid into dimethyl sulphate.

$$O_2S{<}\begin{matrix}Cl\\OH\end{matrix} + CH_3OH = O_2S{<}\begin{matrix}OCH_3\\OH\end{matrix} + HCl$$

$$2O_2S{<}\begin{matrix}OCH_3\\OH\end{matrix} = O_2S(OCH_3)_2 + H_2SO_4$$

In place of chlorosulphonic acid, sulphur trioxide may be used. Diethyl sulphate may be prepared in a similar manner. Both substances are used for alkylating hydroxyl and amino groups, *i.e.* replacing the hydrogen by a methyl or ethyl radical (p. 457). Dimethyl sulphate is a colourless liquid, which, both in the liquid state and in the form of vapour, is excessively poisonous. It boils at 188°.

The action of the alkyl halide on the silver salt may also be used in the preparation of a dialkyl sulphate using silver sulphate and an alkyl iodide (see p. 182)—

$$Ag_2SO_4 + 2C_2H_5I = \underset{\text{Diethyl sulphate.}}{SO_2(OC_2H_5)_2} + AgI.$$

Ethyl Hydrogen Sulphate, *Sulphovinic acid.*—The most common method for preparing the esters of inorganic acids is to act upon the alcohol with the inorganic acid. Strong sulphuric acid, however, forms the acid, not the neutral sulphate. Ethyl alcohol and sulphuric acid give, on heating, ethyl hydrogen sulphate—

$$C_2H_5OH + H_2SO_4 = \underset{\text{Ethyl hydrogen sulphate.}}{SO_2(OH)(OC_2H_5)} + H_2O.$$

The acid sulphates are very unstable. They are decomposed on heating with both alcohol and water. With the former, ether is produced, with the latter, hydrolysis occurs, and alcohol and sulphuric acid are formed—

$$C_2H_5{\cdot}H{\cdot}SO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4.$$
$$C_2H_5{\cdot}H{\cdot}SO_4 + H_2O = C_2H_5OH + H_2SO_4.$$

The acid sulphates form salts with metallic bases, which are comparatively stable substances, being undecomposed by boiling water or alkalis; but they are hydrolysed by acids, which liberate the unstable acid ester. The general formula of these salts is $RM'{\cdot}SO_4$, in which R stands for the radical and M for the metal. The calcium and barium salts are soluble, and the metal is not immediately precipitated by sulphuric acid.

EXPT. 68. *Preparation of Potassium Ethyl Sulphate.*—Forty c.c. of pure ethyl alcohol and 10 c.c. of strong sulphuric acid are heated in a flask on the water-bath for half an hour, then poured into a basin containing 100 c.c. of water, and chalk added in excess. The calcium salt is thereby formed. The mixture is boiled and filtered. Potassium carbonate (about 25 grams) in solution is added, until the liquid is alkaline. This precipitates the calcium as carbonate, and the potassium salt remains in solution. The solution is filtered and evaporated to a very small volume when potassium ethyl sulphate crystallises out on cooling.

The following equations express the chemical reactions which occur:—

1. $C_2H_5OH + H_2SO_4 = \underset{\text{Ethyl hydrogen sulphate.}}{C_2H_5{\cdot}H{\cdot}SO_4} + H_2O.$
2. $2C_2H_5{\cdot}H{\cdot}SO_4 + CaCO_3 = \underset{\text{Calcium ethyl sulphate.}}{(C_2H_5SO_4)_2Ca} + H_2O + CO_2.$
3. $(C_2H_5SO_4)_2Ca + K_2CO_3 = \underset{\text{Potassium ethyl sulphate.}}{2C_2H_5{\cdot}K{\cdot}SO_4} + CaCO_3$

Potassium ethyl sulphate in solution gives no precipitate with barium chloride as the barium salt is soluble; but if the salt is first boiled with a little dilute hydrochloric acid, the ethyl sulphuric acid is decomposed giving ethyl alcohol and free sulphuric acid, which now reacts with barium chloride (see above).

$$C_2H_5KSO_4 + HCl = C_2H_5HSO_4 + KCl$$
$$C_2H_5HSO_4 + H_2O = C_2H_5OH + H_2SO_4.$$

Ethyl Nitrate.—The nitrates are prepared by the action of strong nitric acid on the alcohols. Ethyl alcohol and nitric acid give ethyl nitrate and water—

$$C_2H_5OH + HO{\cdot}NO_2 = \underset{\text{Ethyl nitrate.}}{C_2H_5O{\cdot}NO_2} + H_2O.$$

But oxidation of the alcohol may occur at the same time, the nitric acid being reduced to nitrous acid, which combines with the alcohol to form a nitrous ester. To avoid the formation of ethyl nitrite, a quantity of urea is added, which destroys any nitrous acid that may be formed. The urea and nitrous acid react, with the production of free nitrogen, carbon dioxide, and water (p. 337)—

$$\underset{\text{Urea.}}{CON_2H_4} + 2HNO_2 = CO_2 + 2N_2 + 3H_2O.$$

EXPT. 69. *Preparation of Ethyl Nitrate.*—Twenty c.c. of concentrated nitric acid (sp. gr. 1·4) are poured into a retort attached to a condenser and receiver. Five grams of urea are then introduced, and 50 c.c. of pure ethyl alcohol are gradually added from a tap-funnel. The mixture is then slowly distilled from the water-bath. The ethyl nitrate boils at 86°. The substance is liable to explode when quickly heated. When reduced with tin and hydrochloric acid, ethyl nitrate yields hydroxylamine and ethyl alcohol—

$$C_2H_5{\cdot}O{\cdot}NO_2 + 3H_2 = C_2H_5OH + NH_2OH + H_2O.$$

Ethyl and Amyl Nitrite.—The nitrites are obtained by passing nitrogen trioxide into the alcohol, or more conveniently by adding sulphuric acid or hydrochloric acid to a mixture of the alcohol and sodium nitrite, whereby nitrous acid is liberated. Ethyl and amyl nitrite may be prepared this way—

$$\underset{\text{Amyl alcohol.}}{C_5H_{11}OH} + HO{\cdot}NO = \underset{\text{Amyl nitrite.}}{C_5H_{11}{\cdot}ONO} + H_2O.$$

EXPT. 70. *Preparation of Ethyl Nitrite.*—In a distilling flask of about 700 c.c. capacity and fitted with a dropping funnel, 100 grams of sodium nitrite are dissolved in sufficient water (about 160 c.c.) so that the addition of 75 c.c. of ethyl alcohol gives no precipitate. Hydrochloric acid (20 per cent.) is now run in at a moderate rate, the flask being occasionally shaken. Ethyl nitrite is evolved in a steady stream and is liquefied by passing it through a U-tube immersed in crushed ice.

Preparation of Amyl Nitrite.—Ten grams of amyl alcohol and 10 grams of finely powdered sodium nitrite are mixed together in a flask and cooled in ice, whilst 6 grams of strong sulphuric acid are added.

A little water is then poured in, when the amyl nitrite floats as a yellow liquid on the surface, and may be removed, dehydrated over calcium chloride, and distilled. Amyl nitrite boils at 96°. Both ethyl and amyl nitrite are used medicinally in cases of heart disease.

Sweet Spirits of Nitre is prepared by distilling a mixture of alcohol, sulphuric acid, nitric acid, and copper turnings. The reaction is a complex one, and gives rise to the formation of ethyl nitrite, aldehyde, acetic ether, and acetic acid. The copper probably attacks the nitric acid, forming nitrous acid, which reacts with the alcohol, and gives ethyl nitrite, whilst the products of oxidation are produced by the action of nitric acid on the alcohol. Spirits of nitre is used in medicine.

EXPT. 71.—*Preparation of Sweet Spirits of Nitre.*—Mix together 20 c.c. of alcohol and 2 c.c. of concentrated sulphuric acid, and cool. Pour the mixture into a retort attached to a condenser and receiver, and add 3 c.c. of nitric acid. Finally, introduce 4 grams of copper in small pieces, and distil gently from the water-bath. The distillate, diluted with about 3 times its volume of spirts of wine, forms sweet spirits of nitre.

The Alkyl Halides.—It should be remembered that the alkyl halides, like ethyl chloride, bromide, and iodide, may be regarded as esters of the halogen acids, both from the point of view of their mode of preparation and from their behaviour with alkalis.

THE NITRO-PARAFFINS

The nitro-paraffins are isomeric with the nitrites. They both possess the general formula $R{\cdot}NO_2$. The nitrites are prepared, as we saw above, by the action of nitrous acid on the alcohol; the nitro-paraffins are obtained by distilling a mixture of the alkyl iodide with silver nitrite. Ethyl iodide and silver nitrite give nitroethane, together with some ethyl nitrite—

$$C_2H_5I + AgNO_2 = C_2H_5NO_2 + AgI.$$

EXPT. 72. *Preparation of Nitroethane.*—The silver nitrite required is prepared by adding a solution of silver nitrate to the equivalent amount of pure sodium nitrite dissolved in water. The precipitate is washed and thoroughly dried. The silver nitrite (5 grams) mixed with its own weight of dry sand is placed in a small distilling flask, attached to a condenser. The ethyl iodide (5 grams) is added gradually

through a tap-funnel inserted tightly into the neck of the distilling flask. When the ethyl iodide is added, a considerable rise of temperature occurs. The contents of the flask are then distilled. To show the formation of ethyl nitrolic acid (see below), the liquid is dissolved in a little caustic potash solution, and a solution of potassium nitrite added. On cautiously adding dilute sulphuric acid, a deep red coloration appears. If acid is added until the potassium salt of the nitrolic acid is decomposed, the colour vanishes again.

The nitro-paraffins are colourless, pleasant-smelling liquids the boiling-points of which are much higher than those of the corresponding nitrous esters.

		Boiling-point.		Boiling-point.
CH_3NO_2	Methyl nitrite	$-12°$	Nitromethane	101°
$C_2H_5NO_2$	Ethyl nitrite	16°	Nitroethane	114°

The difference in the structure of the two groups of compounds is clearly indicated by their behaviour with caustic alkalis and with reducing agents.

Caustic alkalis dissolve the primary nitro-paraffins (p. 194) forming salts, whereas the alkyl nitrites are hydrolysed, and yield the alcohol and salt of nitrous acid—

$$\underset{\text{Nitroethane.}}{C_2H_5NO_2} + KOH = \underset{\text{Potassium nitroethane.}}{C_2H_4KNO_2} + H_2O.$$

$$\underset{\text{Ethyl nitrite.}}{C_2H_5NO_2} + KOH = C_2H_5OH + KNO_2.$$

With reducing agents the nitro-paraffins lose their oxygen, which is replaced by two atoms of hydrogen, and are converted into amines (p. 205); the alkyl nitrites are decomposed into alcohol on the one hand, and into hydroxylamine or ammonia on the other—

$$\underset{\text{Nitroethane.}}{C_2H_5NO_2} + 3H_2 = \underset{\text{Ethylamine.}}{C_2H_5NH_2} + 2H_2O.$$

$$\underset{\text{Ethyl nitrite.}}{C_2H_5NO_2} + 2H_2 = C_2H_5OH + NH_2OH.$$

These differences are accounted for by supposing that the nitrogen in the nitro-paraffins is directly linked to the carbon atom of the alkyl group, whilst in the nitrites the acid radical is attached

to the carbon atom of the alkyl group by oxygen. The structural formula for nitroethane contains a semipolar double bond (p. 379).

$$CH_3{\cdot}CH_2{\cdot}N\begin{matrix}\nearrow O\\ \searrow\!\!\!= O\end{matrix} \qquad CH_3{\cdot}CH_2{\cdot}O{\cdot}N{:}O.$$

Nitroethane. Ethyl nitrite.

Direct nitration of secondary and tertiary paraffins is sometimes possible with dilute or concentrated nitric acid, but the yields are seldom good. Another method is by the action of alkali nitrite on α-halogen fatty acids and elimination of CO_2 by warming.

$$CH_3CHCl{\cdot}COOH + KNO_2 \longrightarrow CH_3CHNO_2{\cdot}COOH \longrightarrow CH_3{\cdot}CH_2NO_2$$

Distinction between Primary, Secondary, and Tertiary Alcohols.—The action of nitrous acid on the nitro-paraffins is used as a means of distinguishing the primary, secondary, and tertiary alcohols, and is known as *Victor Meyer's method*. By converting the alcohols into the corresponding alkyl iodides, and distilling the latter with silver nitrite, primary, secondary, and tertiary nitro-paraffins are produced, containing the following groups :—

$$-CH_2{\cdot}NO_2 \qquad =CH{\cdot}NO_2 \qquad \equiv C{\cdot}NO_2.$$

Primary. Secondary. Tertiary.

With nitrous acid the primary nitro-paraffins form acids known as **nitrolic acids**, which dissolve in alkalis, forming salts with a dark red colour. Nitroethane gives ethyl nitrolic acid—

$$\begin{array}{l} CH_3{\cdot}C\boxed{H_2}{\cdot}NO_2 \\ \quad + \boxed{O}NOH \end{array} = \begin{array}{c} CH_3{\cdot}C{\cdot}NO_2 \\ \| \\ NO\mathbf{H}. \end{array} + H_2O.$$

Ethyl nitrolic acid.

The hydrogen indicated by thick type is replaceable by a metal. The secondary nitro-paraffins, like secondary nitropropane, form, with nitrous acid, substances which dissolve in alcohol, ether, or chloroform, with a blue colour, and are known as **pseudo-nitrols.** They are not acids and form no salts.

$$\begin{array}{l} (CH_3)_2C\boxed{H}\,NO_2 \\ \quad + NO\boxed{OH} \end{array} = \begin{array}{c} (CH_3)_2C{\cdot}NO_2 \\ | \\ NO. \end{array} + H_2O.$$

Isopropyl pseudo-nitrol.

The tertiary nitro-paraffins do not react with nitrous acid.

Questions on Chapter XII

1. Describe a method for the preparation and purification of ethyl acetate.

2. In what respect does the action of a metallic base (*e.g.* caustic soda) on an acid differ from that of an alcohol on an organic acid?

3. Explain the action of (1) caustic potash, (2) ammonia, and (3) sodium on acetic ester.

4. How could you distinguish an acid from an ester, both of which had the same molecular formula, $C_4H_8O_2$? How would you determine the nature of the acid and alcohol combined in an ester of the above formula?

5. Why is ethyl chloride to be regarded as an ester?

6. How would you distinguish between the following isomeric compounds: nitroethane and ethyl nitrite?

7. How is "sweet spirits of nitre" prepared? What substances does it contain?

8. Describe V. Meyer's method for identifying primary, secondary, and tertiary alcohols.

9. Describe and illustrate three methods of preparing, (1) esters of organic acids, (2) esters of inorganic acids. What is meant by *equilibrium constant* applied to the process of esterification, how is it determined, and how can the percentage amount of ester be ascertained for any known mixture of acid and alcohol?

10. Describe the action of water upon ethyl acetate, acetic anhydride, acetyl chloride, and ethyl chloride.

11. By what reactions would you obtain the following derivatives from acetic acid; acetyl chloride, acetamide, ethyl acetate, acetic anhydride, monochloracetic acid?

12. How is ethyl acetate prepared, and what is its constitutional formula? Explain clearly why the action of caustic soda on ethyl acetate has been called saponification.

13. The nitrites and the nitro-compounds are regarded as isomeric; what is the ground for this? Contrast the chief reactions of one member of each of these groups.

14. Explain the terms "mass law" and "equilibrium point." Given the concentration of alcohol and acid how would you calculate the amount of ester formed at a given temperature?

CHAPTER XIII

SULPHUR COMPOUNDS

In the list of reactions on p. 84 it will be seen (Reaction 9) that the alkyl halides combine with potassium hydrosulphide, and yield compounds similar in composition to the alcohols, but containing sulphur in place of oxygen. These substances are termed *thio-alcohols* or **mercaptans.** If potassium sulphide, K_2S, is used in place of the hydrosulphide, the *alkyl sulphides* or **thio-ethers** are formed. A third class of compounds is known as the **disulphides,** and corresponds to sodium disulphide, Na_2S_2, which also have representatives among the alkyl oxides. The mercaptans, thio-ethers, and disulphides may be compared with the alcohols, ethers, and peroxides on the one hand, and with the sulphur compounds of sodium on the other.

The ethyl compounds may be taken as illustrating this relation—

C_2H_5OH Ethyl alcohol.	C_2H_5SH Ethyl hydrosulphide.	$NaSH$ Sodium hydrosulphide.
$O\langle^{C_2H_5}_{C_2H_5}$ Ethyl ether.	$S\langle^{C_2H_5}_{C_2H_5}$ Ethyl sulphide.	$S\langle^{Na}_{Na}$ Sodium sulphide.
$\begin{array}{l}O—C_2H_5\\ \vert\\ O—C_2H_5\end{array}$ Ethyl peroxide.	$\begin{array}{l}S—C_2H_5\\ \vert\\ S—C_2H_5\end{array}$ Ethyl disulphide.	$\begin{array}{l}S—Na\\ \vert\\ S—Na\end{array}$ Sodium disulphide.

Mercaptans.—The mercaptans are prepared (1) by the action of potassium hydrosulphide on the alkyl halide; (2) by distilling a solution of potassium alkyl sulphate with potassium hydrosulphide; or (3) by acting on the alcohol with phosphorus pentasulphide. Ethyl mercaptan may be obtained by any of these reactions, which are represented by the following equations :—

$$1.\ C_2H_5\boxed{Cl + K}SH = \underset{\text{Ethyl mercaptan.}}{C_2H_5SH} + KCl$$

$$2.\ SO_2\langle^{O\boxed{C_2H_5 + SH}K}_{OK} = C_2H_5SH + K_2SO_4.$$

$$3.\ 5C_2H_5{\cdot}OH + P_2S_5 = 5C_2H_5{\cdot}SH + P_2O_5.$$

Ethyl mercaptan is now used in the manufacture of *sulphonal* (p. 278), and is prepared by heating ethyl chloride with a strong solution of potassium hydrosulphide under pressure in closed vessels. It boils at 36°.

The mercaptans are volatile liquids (with the exception of methyl mercaptan, which is a gas) and are insoluble in water. They possess an intolerable smell. Sodium and potassium liberate hydrogen from the mercaptans, forming mercaptides, which correspond to the alcoholates of these metals. When a mercaptan is added to mercuric oxide, or to an alcoholic solution of mercuric chloride, a crystalline mercury mercaptide is formed. This characteristic compound with mercury has given rise to the name mercaptan (*mercurium*, mercury; *captans*, seizing).

The sodium, potassium, and mercury mercaptides of ethyl have the following formulæ:—

C_2H_5SNa	C_2H_5SK	$(C_2H_5S)_2Hg$
Sodium mercaptide.	Potassium mercaptide.	Mercury mercaptide.

When exposed to the air, the mercaptans are converted into disulphides—

$$\underset{\text{Ethyl mercaptan.}}{\begin{matrix} C_2H_5S\,H \\ C_2H_5S\,H \end{matrix}} + O = \underset{\text{Ethyl disulphide.}}{\begin{matrix} C_2H_5S \\ | \\ C_2H_5S \end{matrix}} + H_2O.$$

The same result is produced by the action of iodine on sodium mercaptide—

$$2C_2H_5SNa + I_2 = C_2H_5S{\cdot}S{\cdot}C_2H_5 + 2NaI.$$

Sulphonic Acids and Sulphonates.—When the mercaptans are oxidised with strong nitric acid, sulphonic acids are formed. Ethyl mercaptan gives ethyl sulphonic acid—

$$C_2H_5SH + 3O = \underset{\text{Ethyl sulphonic acid.}}{C_2H_5SO_3H.}$$

The sulphonates of the alkalis are obtained by the action of the alkyl halides on the alkaline sulphites—

$$C_2H_5\boxed{I + K}SO_3K = \underset{\text{Ethyl potassium sulphonate.}}{C_2H_5SO_3K} + KI.$$

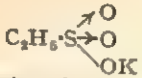
The sulphonic acids are strong monobasic acids, which are very soluble in water, and form soluble salts with the metals.

The aromatic hydrocarbons, like benzene, offer a great contrast to the paraffins in their behaviour with strong sulphuric acid. The aromatic hydrocarbons readily form sulphonic acids. Benzene yields benzene sulphonic acid on heating with strong sulphuric acid—

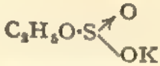
$$\underset{\text{Benzene.}}{C_6H_6} + H_2SO_4 = \underset{\text{Benzene sulphonic acid.}}{C_6H_5{\cdot}SO_3H} + H_2O.$$

whereas the paraffins are acted upon only in a few cases, and then very slowly with fuming sulphuric acid.

The alkyl sulphonates are isomeric with the alkyl sulphites, from which, however, they may be readily distinguished by boiling with caustic potash. The sulphites are hydrolysed into alcohol and potassium sulphite, whereas the sulphonates are unchanged. For this reason the formulæ of the two classes of compounds are represented as follows: In the sulphonates, the sulphur is directly linked to carbon, but in the sulphites the acid radical is united by oxygen to the alkyl group which is characteristic of the esters of all oxygen acids (p. 182). The arrows denote semipolar double bonds (Ch. XXIV).



Potassium ethyl sulphonate.



Potassium ethyl sulphite.

Thio-ethers.—The alkyl sulphides, or thio-ethers, may be prepared by the action of phosphorus pentasulphide on the ethers—

$$5(C_2H_5)_2O + P_2S_5 = \underset{\text{Ethyl sulphide.}}{5\ C_2H_5)_2S} + P_2O_5,$$

or by the action of potassium sulphide on the alkyl halide or alkyl potassium sulphate—

$$2C_2H_5I + K_2S = (C_2H_5)_2S + 2KI.$$

$$\underset{\text{Ethyl potassium sulphate.}}{2SO_2\begin{cases} OC_2H_5 \\ OK \end{cases}} + K_2S = \underset{\text{Ethyl sulphide.}}{(C_2H_5)_2S} + 2K_2SO_4.$$

The alkyl sulphides are insoluble in water, like the mercaptans, and also possess a disagreeable smell.

When ethylene is brought in contact with sulphur chloride it

combines directly with the separation of sulphur forming dichlorodiethyl sulphide, the so-called *mustard gas* of the war.

$$2C_2H_4 + S_2Cl_2 = S(C_2H_4Cl)_2 + S$$

The sulphides combine with the alkyl iodides and form compounds known as *sulphonium iodides*. Ethyl sulphide and ethyl iodide from triethylsulphonium iodide—

$$(C_2H_5)_2S + C_2H_5I = \underset{\text{Triethylsulphonium iodide.}}{(C_2H_5)_3SI.}$$

The iodine of the sulphonium iodide may be exchanged for hydroxyl by the action of moist silver oxide—

$$(C_2H_5)_3S{\cdot}I + AgOH = \underset{\text{Triethylsulphonium hydroxide.}}{(C_2H_5)_3S{\cdot}OH} + AgI.$$

The *sulphonium hydroxides* are hygroscopic crystalline substances which are soluble in water, and the solution has an alkaline reaction. They precipitate metallic oxides from solutions of their salts, absorb carbon dioxide from the air, and behave in fact like the caustic alkalis or ammonia. By introducing three different radicals into the sulphonium iodide, asymmetric sulphur compounds showing optical activity have been obtained (p. 116).

Questions on Chapter XIII

1. Describe a method for the preparation of ethyl mercaptan.

2. What are the characteristic properties of mercaptans? In what respects do they resemble the alcohols?

3. Compare the action of sulphuric acid on the paraffins and on benzene. How are alkyl sulphonic acids prepared?

4. How would you distinguish potassium ethyl sulphonate from potassium ethyl sulphite?

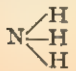
5. Which sulphur compounds resemble ammonia? How are they prepared?

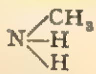
6. How is mercaptan obtained and identified? Describe the action of nitric acid upon it, and state any facts which indicate the constitution of the chief product.

CHAPTER XIV

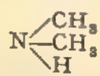
THE AMINES

The Amines.—The name amine is given to derivatives of ammonia in which one or more atoms of hydrogen are replaced by alkyl groups. They are also called *substituted*, or *compound*, ammonias, and from their resemblance to ammonia and the caustic alkalis generally, constitute one of the groups of **organic bases.** If one, two, and three atoms of hydrogen in ammonia are replaced by alkyl groups, the compounds are known as mono-, di-, and tri-alkylamines, and also by the names, *primary*, *secondary*, and *tertiary* amines. The methyl derivatives of ammonia have the following structural formulæ and names :—

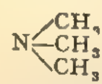




Methylamine
(Primary amine).



Dimethylamine
(Secondary amine).



Trimethylamine
(Tertiary amine).

Although the existence of substituted ammonias was foretold by Liebig as early as 1842, it was not until 1849 that Wurtz prepared the first member, methylamine, by boiling the methyl ester of cyanic acid, or methyl isocyanate (p. 206), with caustic potash. He found that the gas evolved had a strong ammoniacal smell, but differed from ammonia in being inflammable—

$$\underset{\text{Methyl isocyanate.}}{CH_3N{:}\boxed{CO + O}}H_2 = \underset{\text{Methylamine.}}{CH_3NH_2} + CO_2.$$

EXPT. 73.—Mix together in a hard glass test-tube one part of methylamine hydrochloride and two parts of quicklime or soda-lime and heat. The methylamine gas which is evolved may be ignited, and burns with a lambent bluish flame.

The carbon dioxide forms potassium carbonate with the potash present, and the methylamine is liberated as a gas.

Properties of the Amines.—The amines have properties like

those of ammonia. The hydrochloride, nitrate, and sulphate of methylamine are similar in composition to the salts of ammonia—

$\left[CH_3{\cdot}NH_3\right]^{+}Cl'$	$\left[CH_3{\cdot}NH_3\right]^{+}NO_3'$	$\left[CH_3{\cdot}NH_3\right]_2^{2+}SO_4''$
Methylamine hydrochloride.	Methylamine nitrate.	Methylamine sulphate.

The amines also form double salts with the chlorides of platinum, gold, and mercury. The platinum salts of the amines are yellow, crystalline substances, closely resembling in appearance ammonium chloroplatinate, and they are similarly constituted. Methylamine chloroplatinate has the formula—

$$\left[CH_3{\cdot}NH_3\right]_2^{2+}PtCl_6''.$$

The platinum salts are readily prepared by dissolving the amine in moderately strong hydrochloric acid and adding platinic chloride. These salts often serve for determining the molecular weight of the amine (p. 46).

The lower members of the series of amines, like methylamine, dimethylamine, and trimethylamine, are gases, which dissolve in water; the higher members are either colourless liquids or solids, the solubility of which rapidly decreases with increasing molecular weight. The more volatile amines have a strong ammoniacal smell.

As the hydrochlorides and nitrates of the amines are very soluble in water, amines, which are themselves insoluble, dissolve readily on the addition of dilute hydrochloric or nitric acid.

The following table contains a list of the first four members of the series, from which it will be observed that the boiling-points generally rise from the primary to the tertiary amines :—

Amine.	Primary. Boiling-point.	Secondary. Boiling-point.	Tertiary. Boiling-point.
Methylamine	$-6°$	$7°$	$3{\cdot}5°$
Ethylamine	$19°$	$56°$	$90°$
Propylamine . . .	$49°$	$98°$	$156°$
Butylamine	$76°$	$160°$	$215°$

Primary, Secondary, and Tertiary Amines.—It has already been stated that the amines are divided into three classes, which are

termed primary, secondary, and tertiary amines, according to whether one, two, or three hydrogen atoms in ammonia are replaced by radicals.

Each of these classes possesses certain distinctive properties by which it may be identified. The methods of identification depend upon the presence of certain groups—in reality, upon the number of hydrogen atoms of ammonia unsubstituted by radicals.

These groups may be termed primary or **amino** groups, secondary or **imino** groups, and tertiary or nitrile groups—

$-NH_2$	$=NH$	$\equiv N$
Primary, or amino group.	Secondary, or imino group.	Tertiary, or nitrile group.

Nitrous acid is one reagent employed for distinguishing the three groups.

The primary amines combine with nitrous acid and form soluble nitrites, which resemble ammonium nitrite in being rapidly decomposed in presence of excess of nitrous acid. But, whereas ammonium nitrite yields water and nitrogen, the primary amine forms an alcohol, water, and nitrogen. Methylamine nitrite decomposes in aqueous solution into methyl alcohol, water, and nitrogen. The action of primary aromatic amines is more complex.

$$\begin{array}{r|c|l} H & N & H_2 \\ HO & N & O \end{array} = H_2O + N_2 + H_2O$$

Ammonium nitrite.

$$\begin{array}{r|c|l} CH_3 & N & H_2 \\ HO & N & O \end{array} = CH_3{\cdot}OH + N_2 + H_2O.$$

Methylamine nitrite.

This reaction is most conveniently carried out by dissolving the amine, or its salt, in dilute hydrochloric acid, and then adding a solution of sodium nitrite. Effervescence at once begins on warming, and nitrogen is evolved. Alcohol is then found in solution. If the same reaction is applied to a secondary amine, no effervescence occurs on addition of sodium nitrite, but a yellow oil separates, which is called a *nitrosamine*, and is volatile in steam

(p. 421). Dimethylamine forms dimethyl nitrosamine. It is formed by the following reaction—

$$(CH_3)_2N\boxed{H + HO}NO = (CH_3)_2N{\cdot}NO + H_2O.$$

Dimethyl nitrosamine.

EXPT. 74.—For this experiment methylaniline, $C_6H_5NHCH_3$, may be used. Dissolve the base in dilute hydrochloric acid by shaking, and add to the clear solution a few drops of sodium nitrite. An emulsion consisting of oily drops of the nitrosamine,

$$C_6H_5N(NO)CH_3$$

is formed, which on shaking with ether dissolves and gives a yellow solution.

Nitrous acid is without action on the tertiary amines. The action of nitrous acid may therefore be employed for the preparation of tertiary amines free from secondary or primary compounds. If after the addition of sodium nitrite to the acid solution of the amines the product is distilled in steam, the alcohol derived from the primary amine and the nitrosamine of the secondary amine are removed; the tertiary amine remains as the hydrochloride in the distilling vessel. The nitrosamine may be converted on boiling with strong hydrochloric acid into the secondary amine—

$$(CH_3)_2N{\cdot}NO + 2HCl = (CH_3)_2NH{\cdot}HCl + NOCl,$$

but the primary amine cannot be recovered. Another method for separating the three groups of amines is described below.

Primary amines may also be identified by means of the isocyanide, or carbamine reaction described on p. 227. In the reaction referred to, chloroform is detected by the smell of phenylisocyanide evolved on heating chloroform with aniline and alcoholic potash. Any primary amine may be substituted for aniline, with the formation of the corresponding alkyl isocyanide. Methylamine forms, with chloroform and potash, methyl isocyanide; ethylamine gives ethyl isocyanide, and they all possess the same disagreeable smell—

$$CH_3N\boxed{H_2} + C\boxed{HCl_3} + 3KOH = CH_3{\cdot}NC + 3KCl + 3H_2O.$$

Methyl isocyanide.

Secondary and tertiary amines do not form isocyanides. The acid chlorides and anhydrides combine with primary and secondary

amines, and form amides (p. 178); but have no action on the tertiary amines. Acetyl chloride forms, with methylamine and dimethylamine, methyl- and dimethyl acetamide—

$$CH_3{\cdot}CO{\cdot}Cl + NH_2{\cdot}CH_3 = \underset{\text{Methyl acetamide.}}{CH_3{\cdot}CO{\cdot}NH{\cdot}CH_3} + HCl.$$

$$CH_3{\cdot}CO{\cdot}Cl + NH(CH_3)_2 = \underset{\text{Dimethylacetamide.}}{CH_3{\cdot}CO{\cdot}N(CH_3)_2} + HCl.$$

EXPT. 75.—To show the action of acetyl chloride on primary and secondary amines, aniline, $C_6H_5NH_2$, and methylaniline, $C_6H_5NHCH_3$, may be used.

Quaternary Ammonium Compounds.—Although tertiary amines are unchanged by many of the reagents which react with the primary and secondary amines, they possess the distinctive property of uniting with a molecule of an alkyl iodide to form what are known as *quaternary ammonium iodides*. The reaction resembles that by which alkyl sulphides are converted into sulphinium iodides (p. 199). The quaternary compounds are solid substances, which are comparatively stable, and are undecomposed by boiling caustic alkalis. Trimethylamine and methyl iodide form tetramethyl ammonium iodide—

$$N(CH_3)_3 + CH_3I = \underset{\substack{\text{Tetramethyl}\\\text{ammonium iodide.}}}{N(CH_3)_4I.}$$

EXPT. 76.—To show this reaction dimethylaniline, $C_6H_5N(CH_3)_2$, may be used. On warming a mixture of equal volumes of the base and methyl iodide, the solid phenyl trimethyl ammonium iodide separates.

By the action of moist silver oxide, which reacts like silver hydroxide, on the quaternary ammonium iodide, the iodine atom is exchanged for hydroxyl, and the resulting compound is known as a *quaternary ammonium hydroxide*—

$$N(CH_3)_4I + AgOH = \underset{\substack{\text{Tetramethyl}\\\text{ammonium hydroxide.}}}{N(CH_3)_4{\cdot}OH} + AgI.$$

Tetramethyl ammonium iodide gives the corresponding hydroxide. These substances are soluble in water, to which they impart a strongly alkaline reaction. They behave, in fact, like ammonia, but they are almost as strongly ionised in solution as caustic soda. They absorb carbon dioxide from the air.

When the quaternary hydroxides are heated, they are converted into the original tertiary amines. Tetramethyl ammonium hydroxide forms trimethylamine and methyl alcohol. The tetraethyl compound gives triethylamine, ethylene, and water—

$$N(CH_3)_4OH = N(CH_3)_3 + CH_3OH.$$
$$N(C_2H_5)_4OH = N(C_2H_5)_3 + C_2H_4 + H_2O.$$

This is a convenient method for preparing the tertiary base in a pure state and free from primary and secondary amines.

The value of this method, as well as of that described above, will be evident when the following process for preparing the amines has been explained.

Preparation of the Amines.—In the same year in which Wurtz discovered the first of the substituted ammonias, Hofmann introduced an important process for preparing the mono-, di-, and trialkylamines. It consisted in heating the alkyl halide with alcoholic ammonia (alcohol saturated with ammonia) in sealed tubes under pressure. The three classes of amines, as well as the quaternary compounds, are produced together. In the case of methyl iodide, the following series of reactions occurs—

$$NH_3 + CH_3I = \underset{\text{Methylamine hydriodide.}}{CH_3 \cdot NH_2 \cdot HI.}$$

$$CH_3 \cdot NH_2 + CH_3I = \underset{\text{Dimethylamine hydriodide.}}{(CH_3)_2NH \cdot HI.}$$

$$(CH_3)_2NH + CH_3I = \underset{\text{Trimethylamine hydriodide.}}{(CH_3)_3N \cdot HI.}$$

$$(CH_3)_3N + CH_3I = \underset{\text{Tetramethyl ammonium iodide.}}{(CH_3)_4N \cdot I.}$$

The difficulty involved in separating the amines formed by the above process may be avoided by using methods of preparation in which only one kind of amine is produced. The primary amines are obtained either by the method of Wurtz already referred to, or by the reduction of the nitro-paraffins (p. 193) with tin and hydrochloric acid. Nitromethane yields methylamine—

$$\underset{\text{Nitromethane.}}{CH_3NO_2} + 3H_2 = \underset{\text{Methylamine.}}{CH_3NH_2} + 2H_2O.$$

Or, by the reduction of the cyanides with sodium in alcoholic solution, methyl cyanide may be converted into ethylamine—

$$\underset{\text{Methyl cyanide.}}{CH_3CN} + 2H_2 = \underset{\text{Ethylamine.}}{CH_3CH_2NH_2}.$$

The readiest method is to add bromine to the amide of a fatty acid, which is converted into the bromamide. Acetamide yields acetobromamide—

$$\underset{\text{Acetamide.}}{CH_3\cdot CONH_2} + Br_2 = \underset{\text{Acetobromamide.}}{CH_3\cdot CONHBr} + HBr.$$

If the acetobromamide is then warmed with excess of potash, it is converted into methyl isocyanate, which further breaks up, on boiling, into methylamine. In the first reaction the hydrobromic acid is removed from the acetobromamide, which produces methyl isocyanate by atomic rearrangement. The methyl isocyanate is then hydrolysed, as previously described in Wurtz's reaction (p. 200)—

$$\underset{\text{Acetobromamide.}}{CH_3\cdot CON \vdots HBr} + KOH = \underset{\text{Methyl isocyanate.}}{CH_3N\cdot CO} + KBr + H_2O.$$

$$CH_3\cdot N\cdot CO + 2KOH = \underset{\text{Methylamine.}}{CH_3NH_2} + K_2CO_3.$$

The two processes may be combined by heating the amide with an alkaline solution of sodium hypochlorite—

$$CH_3\cdot CO\cdot NH_2 + NaOCl + 2NaOH = CH_3NH_2 + NaCl + Na_2CO_3 + H_2O.$$

EXPT. 77.—Mix together in a ¼ litre flask 2 grams of acetamide and 2 grams of bromine, and then cool and add dilute caustic potash solution until the colour of the bromine vanishes. Now add 6 c.c. of a strong potash solution and warm. There is a brisk effervescence and evolution of methylamine, which has a strong smell of herring brine.

Another method is to pass the vapour of alcohol and ammonia over heated thoria (Sabatier)—

$$CH_3OH + NH_3 = CH_3NH_2 + H_2O.$$

The secondary amines may be obtained pure by the decomposition of certain aromatic bases which will be described under the aromatic compounds (p. 429). Secondary amines are also obtained in considerable quantity together with primary amines by passing the vapour of oximes mixed with hydrogen over heated nickel—

$$CH_3\cdot CH\!:\!NOH = C_2H_5NH_2$$
$$2C_2H_5NH_2 = (C_2H_5)_2NH + NH_3.$$

Two of the methods for the preparation of primary amines may

be utilised for passing from one member of a homologous series to the next.

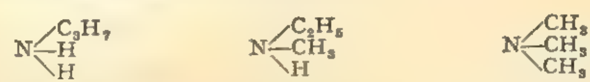
For example, methyl alcohol may be converted into the iodide, the cyanide, and, finally, by reduction, into ethylamine and ethyl alcohol—

$$\underset{\substack{\text{Methyl}\\\text{alcohol.}}}{CH_3OH} \xrightarrow{HI} \underset{\substack{\text{Methyl}\\\text{iodide.}}}{CH_3I} \xrightarrow{KCN} \underset{\substack{\text{Methyl}\\\text{cyanide.}}}{CH_3CN} \xrightarrow{2H_2} \underset{\text{Ethylamine.}}{CH_3{\cdot}CH_2{\cdot}NH_2} \xrightarrow{HNO_2} \underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_5{\cdot}OH.}$$

In order to pass from a higher to a lower member of a series, the second method may be introduced. Ethyl alcohol may be converted into acetic acid, then into acetamide (p. 179), methylamine, and methyl alcohol—

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_5OH} \xrightarrow{O} \underset{\substack{\text{Acetic}\\\text{acid.}}}{C_2H_4O_2} \xrightarrow{NH_3} \underset{\text{Acetamide.}}{C_2H_3O{\cdot}NH_2} \xrightarrow{Br_2+KOH} \underset{\text{Methylamine.}}{CH_3{\cdot}NH_2} \xrightarrow{HNO_2} \underset{\substack{\text{Methyl}\\\text{alcohol.}}}{CH_3OH.}$$

Metameric Amines.—If a primary amine is treated by Hofmann's method with an alkyl iodide in which the alkyl group is different from that present in the amine, a **mixed amine** is formed. A third alkyl group may be introduced, which is again different from the other two. It is easy to conceive how, by this means, metameric amines may result (p. 121). A substance having the formula C_3H_9N represents three metameric substances—propylamine, ethylmethylamine, and trimethylamine—



Propylamine. Ethylmethylamine. Trimethylamine.

Methylamine, CH_3HN_2, *dimethylamine*, $(CH_3)_2NH$, and *trimethylamine*, $(CH_3)_3N$, are gases. They are all present, but chiefly dimethylamine, in the brine in which herrings have been salted, and arise from the putrefaction of the fish.

Dimethylamine and trimethylamine are also present in considerable quantity among the products of the destructive distillation of molasses residues from the beet-root industry, together with other amines and methyl alcohol (p. 303). The amines are separated

by adding hydrochloric acid, distilling off the alcohol, and evaporating the residue to dryness. When di- or tri-methylamine hydrochloride is heated in a current of hydrochloric acid gas, it yields methyl chloride and ammonium chloride—

$$NH(CH_3)_2{\cdot}HCl + 2HCl = 2CH_3Cl + NH_4Cl.$$
$$N(CH_3)_3{\cdot}HCl + 3HCl = 3CH_3Cl + NH_4Cl.$$

The methyl chloride obtained in this way from the beet-root residues is liquefied by compression into steel cylinders, and is used like ethyl chloride in surgery for producing insensibility (p. 82). Its rapid evaporating causes intense cold. Under the receiver of an air-pump the temperature may be reduced to $-55°$. The presence of the methylamine bases in herring brine and molasses residues has its origin in the character of the nitrogenous constituents of animal and vegetable matter, many of which contain these basic groups, which become detached by decomposition.

Methylamine and dimethylamine are conveniently prepared by the action of formaldehyde on ammonium chloride—

$$H{\cdot}COH + NH_4Cl = CH_2{:}NH(HCl) + H_2O$$
$$CH_2{:}NH(HCl) + H_2O + H{\cdot}COH = CH_3NH_2{\cdot}HCl + H{\cdot}CO_2H.$$

The methylamine hydrochloride then reacts in a similar fashion, yielding the dimethylamine salt.

Diamines.—When ammonia acts upon ethylene chloride it combines with it as it does with an alkyl iodide, but both halogen atoms in ethylene chloride are replaced by amino groups and ethylene diamine is produced—

$$\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} + 4NH_3 = \begin{matrix} CH_2{\cdot}NH_2 \\ | \\ CH_2{\cdot}NH_2 \end{matrix} + 2NH_4Cl.$$

Ethylene diamine.

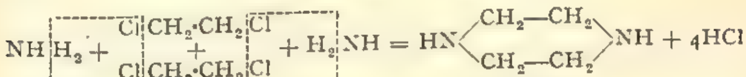
The other alkylene halides behave similarly. These compounds are called *primary diamines*, and are basic substances like the amines. They are also obtained by the reduction of dicyanides by means of sodium in alcoholic solution. Trimethylene cyanide, which is prepared by the action of potassium cyanide on trimethylene bromide, gives, in this way, pentamethylene diamine—

$$\begin{array}{lcl} \mathrm{CN} & & \mathrm{CH_2{\cdot}NH_2} \\ | & & | \\ \mathrm{(CH_2)_3} + 4\mathrm{H_2} & = & \mathrm{(CH_2)_3} \\ | & & | \\ \mathrm{CN} & & \mathrm{CH_2{\cdot}NH_2} \end{array}$$

Trimethylene cyanide. Pentamethylene diamine.[1]

Tetramethylene diamine, or *putrescine,* and pentamethylene diamine, or *cadaverine,* are found in the body after death among the basic products formed by the putrefaction of albumin, and though non-poisonous, are included in the group of compounds known as *ptomaines.*

Ammonia acts upon ethylene chloride in another manner than the one described above. Two molecules of ammonia under certain conditions combine with two molecules of ethylene chloride. The product is a basic substance known as *piperazine.*



Piperazine.

Piperazine forms a soluble salt with uric acid, and has been used in cases of gout and rheumatism.

The following three compounds, which are associated with products of the animal and vegetable organism, and may be regarded as derivatives of ethylene, are sufficiently important to be briefly mentioned. They are known as choline, neurine, and taurine.

Choline is widely distributed in the animal organism, especially in the brain and in egg yolk, forming a curiously complex compound with glycerol, phosphoric acid, and stearic acid, known as *lecithin.*

$$\begin{array}{l} \mathrm{CH_2{\cdot}O{\cdot}OC{\cdot}C_{17}H_{35}} \\ | \\ \mathrm{CH{\cdot}O{\cdot}OC{\cdot}C_{17}H_{35}} \\ | \\ \mathrm{CH_2O{\cdot}PO} \\ \quad \mathrm{HO} \diagup \;\; \diagdown \mathrm{OCH_2{\cdot}CH_2{\cdot}N(CH_3)_3OH} \end{array}$$

Lecithin.

Choline is also found in the seeds of many plants. It is obtained synthetically by the action of trimethylamine on a strong solution of ethylene oxide—

[1] The group $(CH_2)_3$ in the formulæ is an abbreviated form of $'CH_2{\cdot}CH_2{\cdot}CH_2'$ and is known as the *trimethylene* radical to distinguish it from $CH_3{\cdot}CH'{\cdot}CH_2'$, or *propylene* radical.

$$\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\!\!>O + H_2O + N(CH_3)_3 = \begin{array}{l} CH_2OH \\ | \\ CH_2N(CH_3)_3OH. \end{array}$$

Choline.

Choline forms a hygroscopic crystalline mass, which has an alkaline reaction.

Neurine is found among the ptomaines, and is a product of the putrefaction of albumin. It has been obtained synthetically by acting on ethylene bromide with trimethylamine and then treating the product with silver hydroxide—

$$\begin{array}{l} CH_2Br \\ | \\ CH_2{\cdot}N(CH_3)_3Br \end{array} + 2AgOH = \begin{array}{l} CH_2 \\ \| \\ CH{\cdot}N(CH_3)_3OH \end{array} + 2AgBr + H_2O.$$

Neurine.

It may be described as trimethylvinylammonium hydroxide, and has the basic characters of a quaternary ammonium hydroxide (p. 204).

Taurine is present in combination with cholic acid under the name of taurocholic acid in the bile. From its synthesis from *isethionic acid* it must be regarded as aminoethylsulphonic acid, or, seeing that it is a neutral substance, it may be supposed that the basic amino-group neutralises the acid sulphonic group. Its formula is thus represented—

$$\begin{array}{l} CH_2{\cdot}NH_2 \\ | \\ CH_2{\cdot}SO_2{\cdot}OH \end{array} \quad \text{or} \quad \begin{array}{l} CH_2{\cdot}NH_3 \\ | \\ CH_2{\cdot}SO_2 \end{array}\!\!>O.$$

Taurine.

Isethionic acid is obtained from ethyl alcohol and sulphur trioxide, and is hydroxyethylsulphonic acid. By the action of phosphorus pentachloride, the hydroxyl groups are replaced by chlorine, and when the product is boiled with water, chlorethylsulphonic acid is formed. Finally when the last product is heated with ammonia, taurine is obtained. These changes are represented as follows—

$$\underset{\text{Isethionic acid.}}{\begin{array}{l} CH_2OH \\ | \\ CH_2{\cdot}SO_3H \end{array}} \xrightarrow{PCl_5} \underset{\text{Chlorethyl sulphonic chloride.}}{\begin{array}{l} CH_2Cl \\ | \\ CH_2{\cdot}SO_2Cl \end{array}} \xrightarrow{H_2O} \underset{\text{Chlorethyl sulphonic acid.}}{\begin{array}{l} CH_2Cl \\ | \\ CH_2SO_3H \end{array}} \xrightarrow{NH_3} \underset{\text{Taurine.}}{\begin{array}{l} CH_2NH_2 \\ | \\ CH_2SO_3H. \end{array}}$$

Questions on Chapter XIV

1. Give two methods for preparing primary amines free from secondary and tertiary amines.

2. How can a tertiary amine be obtained free from primary and secondary amines?

3. Give a method for distinguishing primary, secondary, and tertiary amines. How would you obtain pure diethylamine from a mixture containing monoethylamine?

4. In what respects do the amines resemble ammonia?

5. Write the formula for the hydrochloride, nitrate, sulphate, and platinochloride of triethylamine.

6. Give the structural formula of metameric amines having the molecular formula $C_4H_{11}N$.

7. Describe the preparation and properties of tetraethyl ammonium hydroxide. What products does it yield on heating?

8. What is the action of acetyl chloride on mono-, di-, and tri-ethylamine?

9. How can (1) acetic acid be converted into formic acid, and (2) methyl alcohol into ethyl alcohol?

10. Describe the technical process for preparing di- and tri-methylamine. For what purpose are they employed?

11. Describe the properties of methylamine, and show how it may be prepared from methyl alcohol, formaldehyde, nitromethane, and acetamide.

12. Starting with ethyl alcohol and with acetic aldehyde respectively, show how ethylamine may be obtained.

13. If given acetamide, describe and explain the method by which you would prepare from it methylamine. How would you convert methylamine into trimethylamine?

14. Describe the reactions by which primary, secondary, and tertiary ethylamines have been obtained. How would you distinguish ethylamine, diethylamine, and triethylamine from each other?

15. Describe the chloroform test for a primary amine, and indicate the nature of the reaction on which it depends.

16. Describe the reactions by which mono- and di-methylamine can be obtained from formaldehyde.

17. Explain the term *primary diamine*, and give an example as well as a method of preparation.

CHAPTER XV

THE CYANOGEN COMPOUNDS

EARLY in the eighteenth century Diesbach, a German colour maker, accidentally discovered Prussian blue by adding a salt of iron to *lixivium sanguinis* (the aqueous extract of blood calcined with potash). In 1782, Scheele obtained **prussic**, or **hydrocyanic, acid** from the lixivium as well as from Prussian blue by distilling them with a mineral acid; but it was not until 1815 that Gay-Lussac explained the composition of hydrocyanic acid and the cyanogen compounds. He showed that these compounds contain the group (CN), to which he gave the name **cyanogen** (κύανος, blue, γεννάω, produce), and pointed out that cyanogen plays the part of an element like chlorine. It was, in fact, the first example of a compound radical (p. 84). We shall see in the course of the chapter the many points of similarity existing between cyanogen and chlorine.

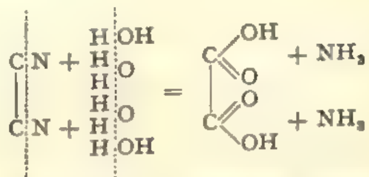
Cyanogen, $(CN)_2$.—Free cyanogen was obtained by Gay-Lussac by heating mercury or silver cyanide—

$$\underset{\text{Mercuric cyanide.}}{Hg(CN)_2} = Hg + \underset{\text{Cyanogen.}}{(CN)_2}.$$

EXPT. 78.—The mercuric cyanide for the experiment is prepared by dissolving mercuric oxide in aqueous hydrocyanic acid and concentrating the solution until it crystallises. Heat a few grams of mercuric cyanide in a hard glass test-tube. A gas is evolved, which may be ignited at the mouth of the tube, and burns with a purple flame. A small quantity of a brown amorphous powder is left, which is known as *paracyanogen*, and is a polymeride of cyanogen. As cyanogen is soluble in water, it must be collected over mercury, should this be necessary.

Cyanogen is a colourless gas with a peculiar smell and is very poisonous. It burns with a purple flame, forming carbon dioxide and nitrogen. Its density corresponds with the formula $(CN)_2$.

Like chlorine, therefore, which in the free state consists of molecules composed of two atoms, the molecule of cyanogen is composed of two cyanogen groups, and the gas is sometimes called *dicyanogen*. Cyanogen may be readily condensed, under a pressure of four atmospheres, to a liquid. Liquid cyanogen boils at − 20° and solidifies at − 34°. Cyanogen dissolves readily in water; but the solution gradually decomposes, forming a brown flocculent precipitate, known as *azulmic acid*, whilst ammonium oxalate is found in solution. The ammonium oxalate arises from the hydrolysis of the cyanogen, a reaction which resembles that which takes place when hydrogen cyanide (p. 212) or the alkyl cyanides are hydrolysed (p. 226)—



Cyanogen. Water. Oxalic acid. Ammonia.
Ammonium oxalate.

Just as methyl cyanide is obtained by dehydrating acetamide (p. 225), so, if oxamide is distilled with phosphorus pentoxide, cyanogen is formed (p. 345)—

$$\underset{\text{Oxamide.}}{\begin{matrix} CO{\cdot}NH_2 \\ | \\ CO{\cdot}NH_2 \end{matrix}} = \underset{\text{Cyanogen.}}{\begin{matrix} CN \\ | \\ CN \end{matrix}} + 2H_2O.$$

If cyanogen is passed into caustic potash solution, it is decomposed into potassium cyanide, potassium cyanate, and water. This reaction brings out clearly the similarity in the properties of cyanogen and the halogens—

$$(CN)_2 + 2KOH = \underset{\substack{\text{Potassium}\\ \text{cyanide.}}}{KCN} + \underset{\substack{\text{Potassium}\\ \text{cyanate.}}}{KCNO} + H_2O.$$

$$Cl_2 + 2KOH = KCl + KClO + H_2O.$$

Hydrocyanic Acid, *Prussic acid,* occurs in certain plants; it is found in the leaves of the cherry laurel, in bitter almonds, and in the kernels of cherry, peach, plum, and other stone fruits. It is

not usually present as the free acid in the plants named, but in combination with glucose (grape-sugar) and benzaldehyde (oil of bitter almonds, p. 474) in the form of a crystalline substance known as *amygdalin*. This crystalline compound is termed a *glucoside*, and is readily decomposed by dilute sulphuric acid into its constituents. The process is one of hydrolysis—

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Benzaldehyde.}}{C_7H_6O} + \underset{\text{Hydrocyanic acid.}}{HCN} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}.$$

The same decomposition is produced by the action of an enzyme (p. 474) known as *emulsin*, which is present in bitter almonds. Emulsin acts only in the presence of water, so that by grinding up bitter almonds with a little water, hydrolysis takes place, and the smell of hydrocyanic acid, together with that of benzaldehyde, is soon perceived. Dilute hydrocyanic acid is usually made by distilling potassium ferrocyanide (see below) with dilute sulphuric acid—

$$\underset{\text{Potassium ferrocyanide.}}{2K_4Fe(CN)_6} + 3H_2SO_4 = \underset{\text{Hydrocyanic acid.}}{6HCN} + \underset{\text{Potassium ferrous ferrocyanide.}}{K_2Fe''Fe(CN)_6} + 3K_2SO_4.$$

The solution slowly decomposes, on standing, into ammonium formate. The reaction is analogous to the formation of ammonium oxalate from cyanogen (p. 211)—

$$HCN + 2H_2O = \underset{\text{Ammonium formate.}}{H{\cdot}CO{\cdot}ONH_4}.$$

EXPT. 79. *Preparation of Hydrocyanic Acid.*—As the acid vapours are excessively poisonous, it is desirable to conduct the following operation in a fume-cupboard. Ten parts of coarsely-powdered potassium ferrocyanide are placed in a retort, and 7 parts of concentrated sulphuric acid, previously diluted with from 10–20 parts of water, are added. The retort is connected with a well-cooled condenser and receiver. On distilling the mixture, aqueous hydrocyanic acid collects in the receiver.

The pure anhydrous acid is prepared by distilling a mixture of powdered potassium cyanide and moderately strong sulphuric acid and passing the vapour, which is evolved, through U-tubes containing solid calcium chloride to remove the water. The dry hydrocyanic acid vapour is then led into a U-tube surrounded by ice, where it condenses to a colourless liquid.

Properties of Hydrocyanic Acid.—Pure hydrocyanic acid boils at 26° and solidifies at − 14°. It is inflammable, and burns with a violet flame. It is excessively poisonous, even in the minutest quantity, and the greatest care should be taken in preparing and in using it.

Pure hydrocyanic acid is rapidly decomposed by strong hydrochloric acid with a considerable rise of temperature, first into formamide, and finally into formic acid and ammonium chloride—

$$\underset{\text{Hydrocyanic acid.}}{HCN} + H_2O = \underset{\text{Formamide.}}{HCO{\cdot}NH_2}.$$

$$HCO{\cdot}NH_2 + H_2O + HCl = \underset{\text{Formic acid.}}{H{\cdot}CO{\cdot}OH} + NH_4Cl.$$

Strong sulphuric acid probably effects the same change, but as it decomposes formic acid at the same time into carbon monoxide (p. 158), no formic acid is actually produced. This explains why carbon monoxide alone is formed when either potassium ferrocyanide or potassium cyanide is heated with strong sulphuric acid.

As hydrocyanic acid yields formamide on hydrolysis, so the reverse process may be effected by removing the elements of water from formamide.

On distilling formamide with phosphorus pentoxide, hydrocyanic acid is produced—

$$HCONH_2 - H_2O = HCN.$$

When an alcoholic solution of hydrocyanic acid is reduced with metallic sodium, methylamine is formed, just as methyl cyanide is converted into ethylamine (p. 226)—

$$HCN + 2H_2 = \underset{\text{Methylamine.}}{CH_3{\cdot}NH_2}.$$

Since hydrocyanic acid yields two series of salts, the cyanides and the isocyanides (p. 227) there is probably dynamic isomerism (p. 330), thus $H{\cdot}C{\vdots}N \rightleftarrows H{\cdot}N{\vdots}C$. This involves a bivalent carbon atom as a quadruple link is impossible. The electronic structure of the cyanide *ion* is identical with that of the isocyanide ion.

The Metallic Cyanides.—Potassium cyanide, KCN, and sodium cyanide, NaCN, are two of the most important salts of hydrocyanic

acid. Potassium cyanide is formed by fusing potassium ferrocyanide alone or with potassium carbonate—

$$1.\ K_4Fe(CN)_6 = \underset{\text{Potassium cyanide.}}{4KCN} + FeC_2 + N_2.$$

$$2.\ K_4Fe(CN)_6 + K_2CO_3 = 5KCN + \underset{\text{Potassium cyanate.}}{KOCN} + CO_2 + Fe.$$

Neither process is used commercially. The large quantity of cyanide demanded for the extraction of gold from gold quartz by the MacArthur-Forrest process (see below) has led to the discovery of new and cheaper methods. When metallic sodium is heated with sodium ferrocyanide, obtained in the coal-gas manufacture, sodium cyanide is formed, and the whole of the cyanogen is obtained as cyanide—

$$Na_4Fe(CN)_6 + Na_2 = 6NaCN + Fe.$$

The fused mass is then filtered from the finely-divided iron. Another important method is to pass ammonia gas over a heated or fused mixture of potassium carbonate and charcoal.

$$2NH_3 + K_2CO_3 + C = 2KCN + 3H_2O.$$

A third method is to pass ammonia over heated sodium. Sodium amide, or *sodamide*, is formed, which is fused and run on to red-hot charcoal. The product is sodium cyanide. The formation of sodium cyanide actually occurs in two stages, sodium cyanamide being first formed (p. 341). The following equations express these reactions—

$$2NH_3 + Na_2 = \underset{\text{Sodamide.}}{2NaNH_2} + H_2$$

$$2NaNH_2 + C = \underset{\text{Sodium cyanamide.}}{CN{\cdot}NNa_2 + 2H_2}$$

$$CN{\cdot}NNa_2 + C = \underset{\text{Sodium cyanide.}}{2NaCN}$$

It has long been known that alkalis when heated with carbon in the presence of free nitrogen form alkali cyanides. The formation of cyanides in the products from blast furnaces is explained in this way. Attempts have been recently made to produce cyanides from the nitrogen of the air by passing air over fused calcium carbide. Calcium carbide, produced from a mixture of powdered

limestone and coke, heated to the high temperature of the electric furnace (p. 260), combines with nitrogen and forms mainly calcium cyanamide. Barium carbide, on the other hand, yields barium cyanide, from which the alkali salts may be prepared—

$$\underset{\text{Barium carbide.}}{BaC_2} + N_2 = \underset{\text{Barium cyanide.}}{Ba(CN)_2}.$$

Other methods are by the action of nitric acid on ammonium thiocyanate (p. 223), giving hydrocyanic acid, which is passed into potash solution and evaporated (Gelée's method), and the distillation of beet-root residues, which yield a certain quantity of hydrocyanic acid (Bueb). The nitrides of silicon and aluminium which are formed at the temperature of the electric furnace yield potassium cyanide on heating with potash.

About 10,000 tons of cyanide are produced annually, of which about one-third is used in the Transvaal for gold extraction.

In addition to the application of potassium and sodium cyanides to gold extraction, potassium cyanide is employed in the preparation of solutions of gold and silver for electroplating. The cyanides of these metals form soluble *double salts* with potassium cyanide (see below). The alkali cyanides are very soluble in water, and the solutions undergo gradual decomposition. The action goes on more rapidly on boiling, ammonia being evolved and formates of the alkalis produced. Potassium and sodium cyanide are readily decomposed by the inorganic and organic acids, and even by so weak an acid as carbonic acid, giving off hydrocyanic acid. The smell which potassium cyanide emits, when exposed to the air, is attributed to the action of carbon dioxide. Like hydrocyanic acid, the alkali cyanides are strong poisons.

Detection of Hydrocyanic Acid and Cyanides.—Owing to the poisonous character of hydrocyanic acid and the soluble cyanides, the detection of the presence of these substances is a matter of importance. The volatility and peculiar smell of hydrocyanic acid render its separation and detection a comparatively simple matter. If nitric acid is added to a soluble cyanide and warmed, hydrocyanic acid is evolved. A drop of silver nitrate solution on a watch-glass or glass rod in contact with the vapour becomes turbid from the formation of silver cyanide. In the same way a drop of ammonium sulphide in contact with hydrocyanic acid vapour is converted into ammonium sulphocyanide, NH_4CNS. If the liquid is somewhat concentrated by warming and

acidified with dilute hydrochloric acid, a blood-red stain is produced on the addition of a drop of ferric chloride (p. 224). A common method of detecting hydrocyanic acid is to boil the liquid, which is first made alkaline with potash, with a few drops of ferrous sulphate and a drop of ferric chloride solution. On acidifying the solution, a precipitate of Prussian blue is formed. If the cyanide is mixed with other substances which would interfere with the reaction, it is first separated by distilling the mixture with the addition of a little non-volatile organic acid like tartaric acid. The distillate which contains the hydrocyanic acid is then submitted to the above tests.

The Double Cyanides.—When a solution of potassium or sodium cyanide is added to the solution of a metallic salt, the metal (with the exception of the alkalis, alkaline earths, and mercury, which form soluble cyanides) is precipitated in the form of the insoluble cyanide. A further addition of potassium cyanide produces a solution of the metallic cyanide. A *double cyanide* is formed. If a mineral acid is now added to the solution, hydrocyanic acid is evolved, and the insoluble cyanide of the metal is reprecipitated. In the case of silver, the addition of potassium cyanide to a solution of silver nitrate produces a precipitate of silver cyanide, AgCN, very similar to silver chloride in appearance, which redissolves on the further addition of potassium cyanide, with the formation of a double cyanide, AgCN·KCN. If nitric acid is now added, silver cyanide is reprecipitated, and hydrocyanic acid is evolved—

$$\underset{\text{Potassium silver cyanide.}}{AgCN\cdot KCN} + HNO_3 = \underset{\text{Silver cyanide.}}{AgCN} + HCN + KNO_3.$$

This reaction is utilised for the quantitative analysis of potassium cyanide. A standard solution of silver nitrate is added to the cyanide until a precipitate is just formed. At this point the amount of silver solution added corresponds to the formation of the double cyanide of silver and potassium; for any additional amount of silver nitrate will decompose some of the potassium cyanide and form a precipitate. Hence, each atom of silver taken represents two molecules of potassium cyanide.

The deposition of silver and gold in electroplating with the double cyanides is explained by the breaking up of the compound into the positive K ions and negative $Ag(CN)_2$ ions. The K ions reduce the double cyanide at the kathode, and silver is deposited—

The $Ag(CN)_2$ ions dissolve fresh silver from the anode, and form 2AgCN, which passes into solution as the double cyanide—

$$\begin{array}{r|l} \text{K (cathode)} & Ag(CN)_2 \text{ (anode)} \\ + KAg(CN)_2 & + Ag \\ = (Ag) + 2KCN & = 2AgCN \end{array}$$
$$= 2KAg(CN)_2.$$

For this reason the double salts are sometimes regarded as salts of the radicals $Ag(CN)_2$ and $Au(CN)_2$.

The MacArthur-Forrest process. In the extraction of gold, from gold-bearing rocks the larger particles of gold are first removed by amalgamation with mercury. To the residue known as *tailings*, in which the gold is in a fine state of division, a very dilute solution of sodium cyanide is added in presence of atmospheric oxygen, or other oxidising agent when the soluble gold sodium cyanide is formed—

$$4NaCN + 2Au + H_2O + O = 2NaAu(CN)_2 + 2NaOH.$$

The gold is then deposited from the solution by electrolysis or by the addition of metallic zinc—

$$2NaAu(CN)_2 + Zn + 2NaOH = 2Au + Zn(OH)_2 + 4NaCN.$$

Nearly 2 million ounces of gold are extracted by this process annually.

There is another class of double cyanides in which the metallic cyanide of the heavy metal is not precipitated from solution by a mineral acid. The formation and properties of this class of double cyanides may be illustrated by the following experiment.

Expt. 80.—Make a fresh solution of ferrous sulphate and add potassium cyanide solution until there is no further brown precipitate of cyanide of iron; boil and filter if necessary. A yellow solution is obtained, which, after cooling, is to be divided into two portions. If dilute hydrochloric acid is added to one portion, there is no precipitate of the original cyanide. If strong hydrochloric acid is added to the second portion, a white precipitate is thrown down. The yellow solution contains potassium ferrocyanide, and the addition of strong hydrochloric acid to the second portion precipitates hydroferrocyanic acid. The reactions which occur are expressed as follows:—

1. $2KCN + FeSO_4 = \underset{\text{Ferrous cyanide.}}{Fe(CN)_2} + K_2SO_4.$

2. $Fe(CN)_2 + 4KCN = \underset{\text{Potassium ferrocyanide.}}{K_4Fe(CN)_6}.$

3. $K_4Fe(CN)_6 + 4HCl = \underset{\text{Hydroferrocyanic acid.}}{H_4Fe(CN)_6} + 4KCl.$

A similar reaction takes place when a solution of a cobalt salt is boiled with excess of potassium cyanide and a few drops of acid. Potassium cobalticyanide, $K_3Co(CN)_6$, is formed, from which cobalt cyanide is not reprecipitated by acids. The separation of cobalt from nickel depends upon this reaction. Nickel forms a double cyanide of the first, cobalt of the second class, so that after boiling the double cyanides of the two metals, and then acidifying, it is only the nickel which is precipitated as cyanide.

It therefore appears that in the second class of double cyanides the metallic cyanide forms an integral part of the acid. Hydroferrocyanic acid, $H_4Fe(CN)_6$, contains the acid radical or negative ion[1] *ferrocyanogen*, $Fe(CN)_6$. Hydroferrocyanic acid is a strong acid, and forms a series of salts, some of which, like the zinc (white), copper (red), and ferric (Prussian blue) salts are insoluble, and have a characteristic colour. They are obtained by adding a solution of a salt of the particular metal to a solution of potassium ferrocyanide. The most important salts are potassium and sodium ferrocyanides.

Potassium Ferrocyanide, or *Yellow prussiate of potash*, $K_4Fe(CN)_6 + 3H_2O$, is the starting-point in the preparation of nearly all the cyanogen compounds. Potassium ferrocyanide was formerly manufactured by fusing in an iron pot nitrogenous animal refuse, such as horns, hoofs, blood, leather scraps, etc., with potassium carbonate. The mass is kept stirred during the operation, and, after cooling, is lixiviated with water. On evaporation, large tabular yellow crystals of potassium ferrocyanide are deposited. A satisfactory explanation of the reaction has not yet been offered.

The salt is now obtained almost exclusively from coal gas. The cyanogen derived from the coal, probably in the form of hydrocyanic acid, is absorbed by alkaline ferrous hydrate before passing to the purifiers, and is converted into *sodium ferrocyanide*—

$$Na_4Fe(CN)_6 + 10H_2O.$$

In other gas-works it passes to the iron oxide of the "purifiers," and is converted into insoluble iron ferrocyanide. Some thiocyanate (p. 223) is also formed. The spent oxide is boiled with lime, and the soluble calcium ferrocyanide, which is formed, is extracted and converted into the sodium or potassium salt by treatment with an alkaline carbonate.

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[1] *Vide* J. Walker, *Introduction to Physical Chemistry*, chap. xxvi. p. 296 (Macmillan).

When heated, potassium ferrocyanide first loses its water of crystallisation and becomes colourless; it then blackens and fuses, forming potassium cyanide and iron carbide (p. 214). Ferric salts added to a solution of the ferrocyanide give a precipitate of ferric ferrocyanide or Prussian blue—

$$\underset{\text{Ferric ferrocyanide, or Prussian blue.}}{Fe'''_4[Fe(CN)_6]_3.}$$

When chlorine is passed into a solution of potassium ferrocyanide, the latter turns a deep red, and on evaporation red crystals of **potassium ferricyanide**, or *red prussiate of potash*, $K_3Fe(CN)_6$, are deposited—

$$2K_4Fe(CN)_6 + Cl_2 = \underset{\text{Potassium ferricyanide.}}{2K_3Fe(CN)_6} + 2KCl.$$

Expt. 81.—The above reaction also takes place on the addition of bromine. Add bromine water in excess to a solution of potassium ferrocyanide and boil off the excess of bromine. The solution may be evaporated, when red crystals of the ferricyanide are obtained. If a drop of ferric chloride is added to the solution of the ferricyanide, no precipitate of Prussian blue is formed; but the solution turns dark brown. The addition of a ferrous salt throws down a blue precipitate, known as *Turnbull's blue*, or ferrous ferricyanide, $Fe''_3[Fe(CN)_6]_2$.

Potassium ferricyanide is occasionally used in alkaline solution as a mild oxidising agent. It decomposes the alkali and liberates oxygen, forming at the same time potassium ferrocyanide, according to the following equation—

$$\underset{\substack{\text{Potassium}\\\text{ferricyanide.}}}{2K_3Fe(CN)_6} + 2KOH = \underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{2K_4Fe(CN)_6} + H_2O + O.$$

When potassium ferrocyanide is heated with moderately strong nitric acid, and then neutralised with caustic soda, **sodium nitroprusside**, $Na_2NOFe(CN)_5 + 2H_2O$, crystallises out on evaporation in the form of ruby-red crystals. Sodium nitroprusside solution is used as a test for sulphur. The sulphur, when present in the form of a soluble sulphide in alkaline solution, produces a deep violet coloration on the addition of sodium nitroprusside solution (p. 19).

Expt. 82.—Heat together on the water-bath for half an hour 4 grams of powdered potassium ferrocyanide and 4 c.c. of strong nitric acid, previously diluted with 5 c.c. of water. Cool the mixture, and

add caustic soda solution until alkaline. Add a few drops of the solution to a test-tube of water, and then a drop of ammonium sulphide. A deep violet coloration is produced.

Cyanogen Chlorides.—When chlorine is passed into hydrocyanic acid, a colourless liquid is produced, which has the formula CNCl, and is known as *liquid cyanogen chloride*—

$$HCN + Cl_2 = CNCl + HCl.$$

It polymerises on standing, forming a solid, $C_3N_3Cl_3$, known as *solid cyanogen chloride* or *cyanuric chloride*.

When treated with potash the liquid cyanogen chloride is converted into potassium cyanate, and the solid into potassium cyanurate—

$$\underset{\text{Cyanogen chloride.}}{CNCl} + 2KOH = \underset{\text{Potassium cyanate.}}{CNOK} + KCl + H_2O.$$

$$\underset{\text{Cyanuric chloride.}}{C_3N_3Cl_3} + 6KOH = \underset{\text{Potassium cyanurate.}}{C_3N_3O_3K_3} + 3KCl + 3H_2O.$$

Cyanic and Cyanuric Acids.—Cyanuric acid, $C_3N_3O_3H_3+2H_2O$, is obtained by a variety of reactions, such as heating urea (see below), alone or in presence of chlorine—

$$\underset{\text{Urea.}}{3CON_2H_4} = \underset{\text{Cyanuric acid.}}{C_3N_3O_3H_3} + 3NH_3.$$

$$6CON_2H_4 + 3Cl_2 = 2C_3N_3O_3H_3 + 4NH_4Cl + 2HCl + N_2,$$

or, it may be obtained by heating in a sealed tube a solution of carbonyl chloride (in an inert solvent like benzene) with ammonia—

$$3COCl_2 + 3NH_3 = C_3N_3O_3H_3 + 6HCl.$$

It is a very stable substance and dissolves unchanged in strong sulphuric acid. The vapour when distilled, cooled in a freezing mixture, is converted into liquid **cyanic acid,** CNOH, which is an extremely unstable substance; for, when warmed to the ordinary temperature, it polymerises with explosive violence, and forms a compound known as *cyamelide,* which undergoes slow transformation into cyanuric acid.

Expt. 83.—The conversion of cyanuric acid into cyanic acid and its reconversion into cyanuric acid was discovered by Wöhler, and offered the first example both of polymerism and of polymerisation

(p. 136). The experiment is readily performed as follows:—Place a few grams of powdered cyanuric acid, which must be previously dehydrated on the water-bath, in a small retort made by blowing a small bulb on the end of a piece of hard, wide glass tubing. The open end of the tube dips to the bottom of a test-tube, which is surrounded by a freezing mixture. The cyanuric acid is heated until it has nearly all disappeared from the bulb. The test-tube is then removed from the freezing mixture. It contains a little liquid cyanic acid. After being exposed to the temperature of the air for a few minutes, it polymerises with a succession of sharp cracks.

Although cyanic acid itself rapidly polymerises, many of its salts are perfectly stable substances.

Potassium Cyanate, CNOK, is obtained by oxidising potassium cyanide. This may be effected by fusing the cyanide with some reducible metallic oxide, like lead or manganese peroxide, or by adding permanganate solution to a solution of potassium cyanide. The use of potassium cyanide as a reducing agent for metallic oxides depends upon this reaction—

$$KCN + O = KOCN.$$

Ammonium Cyanate, $CNO(NH_4)$, may be prepared by bringing together ethereal solutions of ammonia and cyanic acid, cooled in a freezing mixture. It forms a white crystalline powder. If the solid, or a solution in water or alcohol, is heated, an "intramolecular" rearrangement, or change in the positions of the atoms occurs, and the ammonium cyanate is transformed into urea. The nature of this change will be discussed more fully later (p. 341). In the preparation of urea from potassium cyanate, it is only necessary to add ammonium sulphate to the solution of the cyanate in water and evaporate the mixture to dryness. The ammonium cyanate, which is first formed, is thereby converted into urea, which may be extracted from the dried mass with alcohol. The alcohol dissolves the urea, but not the potassium sulphate. The urea crystallises from the alcoholic solution—

$$2CNOK + (NH_4)_2SO_4 = \underset{\text{Ammonium cyanate.}}{2CNO{\cdot}NH_4} + K_2SO_4.$$

$$CNO{\cdot}NH_4 = \underset{\text{Urea.}}{CO(NH_2)_2}.$$

Expt. 84. *Preparation of Potassium Cyanate and Urea.*—Heat 50

grams of pure potassium cyanide in a small iron dish over a large Bunsen burner, and, without waiting for the cyanide to fuse, add gradually 140 grams of red lead. The addition of the lead produces sufficient heat to melt the contents of the dish. When the red lead has been added, and the mixture fuses quietly without effervescence, pour it out on to a cold slab or iron tray—

$$4KCN + Pb_3O_4 = 4CNOK + 3Pb.$$

Powder up the mass, when cold, and separate the potassium cyanate from lead and other impurities by leaving the mass in contact with about 200 c.c. of water for an hour. The solution now contains the potassium cyanate. Filter, and add to the filtrate 50 grams of ammonium sulphate dissolved in water, and evaporate the mixture to dryness on the water-bath. Boil up with about 50 c.c. of methylated spirit on the water-bath, and filter into a crystallising dish. Long prismatic crystals of urea deposit on cooling.

Mercury Fulminate, $C_2N_2O_2Hg + \frac{1}{2}H_2O$, is formed by the action of alcohol on a solution of mercuric nitrate in nitric acid.

EXPT. 85. *Preparation of Mercury Fulminate.*—Three grams of mercury are dissolved in 28 c.c. of strong nitric acid contained in a large flask. The solution is then somewhat cooled, and 43 c.c. of 90 per cent. alcohol are added in two instalments. When the action, which is sometimes very vigorous, has subsided, and the liquid has cooled, colourless needles of mercury fulminate are deposited.

Mercury fulminate was formerly regarded as a nitro-derivative of methyl cyanide; but as it decomposes quantitatively with strong hydrochloric acid into formic acid and hydroxylamine and can be prepared from chloroformoxime, ClCH:NOH, and nitroformoxime, or methyl nitrolic acid, $NO_2CH{:}NOH$, it must be regarded as the mercury salt of carbyloxime, and is therefore isomeric with mercury cyanate

$$\underset{\text{Mercury fulminate.}}{(C{:}NO)_2Hg.}$$

The decomposition into hydroxylamine is represented as follows—

$$\underset{\text{Mercury fulminate.}}{(CNO)_2Hg} + 2HCl + 4H_2O = 2NH_2OH + 2HCO_2H + HgCl_2.$$

The formation of fulminic acid from alcohol is supposed to occur in the following series of steps (Wieland)—

$$CH_3{\cdot}CH_2OH \longrightarrow CH_3{\cdot}CHO \longrightarrow CH{:}NOH{\cdot}CHO \longrightarrow$$
$$CH{:}NOH{\cdot}COOH \longrightarrow C(NO_2){:}NOH{\cdot}COOH \longrightarrow HC(NO_2){:}NOH \longrightarrow$$
$$C{:}NOH + HNO_2$$

Mercury fulminate, when dry, is a powerful explosive, and is used as a detonator. The fulminate is placed in a metal cup in contact with the explosive, and is fired either by a fuse, by electricity, or by a sharp blow.

Other salts of fulminic acid are known, but the free acid has not been isolated. The silver salt, $CNOAg$, was analysed by Liebig (1823), and found to have the same composition as Wöhler's silver cyanate and cyanurate (p. 220). These three salts constituted the first example of substances of the same composition but possessing distinct properties, to which Berzelius applied the term "isomerism."

Thiocyanic Acid and Thiocyanates.—Thiocyanic acid, or sulphocyanic acid, $CNSH$, is separated from its salts by the addition of a mineral acid and is a gas which may be condensed to a liquid in a freezing mixture. The liquid has an acrid and penetrating smell. When removed from the freezing mixture it quickly polymerises like cyanic acid. Ammonium and potassium thiocyanate, or sulphocyanate, have a technical application in cotton dyeing and printing. The potassium salt is obtained by fusing potassium cyanide with sulphur—

$$KCN + S = KCNS.$$

The ammonium salt is prepared by heating carbon bisulphide and ammonia under pressure. Ammonium thiocarbamate is thereby formed—

$$CS_2 + 2NH_3 = SC\begin{cases} NH_2 \\ SH\cdot NH_3. \end{cases}$$

Ammonium thiocarbamate.

When subjected to the action of steam, thiocarbamate is decomposed into ammonium thiocyanate and hydrogen sulphide—

$$SC\begin{cases} NH_2 \\ SHNH_3 \end{cases} = CNS(NH_4) + H_2S.$$

Ammonium thiocyanate.

A certain quantity of ammonium thiocyanate is obtained from gas liquor and "spent oxide," where it is probably formed by the action of sulphur upon ammonium cyanide—

$$NH_4CN + S = NH_4SCN.$$

The soluble thiocyanates are used as a delicate test for iron in the form of ferric salt. When a drop of ferric chloride is added to a solution of potassium or ammonium thiocyanate, an intense red coloration is produced. The colour is due to a compound, resembling potassium permanganate in appearance, which has the formula $Fe(CNS)_3 \cdot 9KCNS + 4H_2O$. The colour disappears if the iron is reduced to the ferrous state.

Mercuric thiocyanate is obtained by adding mercuric chloride to a solution of potassium thiocyanate. The insoluble powder when filtered and dried takes fire on ignition, and forms an exceedingly voluminous ash. When moulded into pellets, dried, and ignited, it produces long snake-like tubes of ash known as "Pharaoh's serpents." The vapour of the burning substance contains mercury and is poisonous.

Esters of the Cyanogen Acids.—Hydrocyanic, cyanic, cyanuric, and thiocyanic acid form a series of esters. Each acid, however, gives rise to, not one, but two isomeric esters, the existence of which is accounted for by differences of structure, which will be presently discussed.

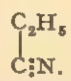
Nomenclature of the Cyanogen Esters.—It will be convenient to give at once the names and structural formulæ of the series of esters above referred to, taking the methyl esters by way of illustration. From hydrocyanic acid are derived **methyl cyanide** and **methyl isocyanide.**

As the alkyl cyanides, like hydrocyanic acid itself, are converted on hydrolysis into the fatty acids (p. 155), they are sometimes designated as the **nitriles** of the corresponding acids.

Hydrocyanic acid is the nitrile of formic acid, methyl cyanide of acetic acid, ethyl cyanide of propionic acid, etc.

Hydrogen cyanide, or Formonitrile.

Methyl cyanide, or Acetonitrile.



Ethyl cyanide, or Propionitrile.

The alkyl isocyanides, which are converted into alkylamines on hydrolysis, are also termed alkyl **carbamines** or carbylamines.

Methyl isocyanide is also known as methyl carbamine—

$$\begin{array}{c} CH_3 \\ | \\ N\vdots C. \end{array}$$

Methyl isocyanide, or Methyl carbamine.

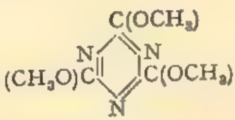
From cyanic acid are derived methyl cyanate and isocyanate or carbimide—

HOCN	$\begin{array}{l} CH_3 \\ \vert \\ O\cdot C\vdots N \end{array}$	$\begin{array}{l} CH_3 \\ \vert \\ N\colon C\colon O \end{array}$
Cyanic acid.	Methyl cyanate.	Methyl isocyanate Methyl carbimide.

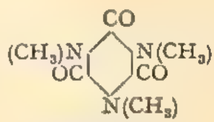
From cyanuric acid, in the same way, methyl cyanurate and isocyanurate are derived, to which the following structural formulæ have been assigned—

$H_3O_3C_3N_3$

Cyanuric acid.



Methyl cyanurate.



Methyl isocyanurate.

Finally, thiocyanic acid gives rise to two esters, methyl thiocyanate and methyl isothiocyanate. The latter is also known as methyl mustard oil, seeing that the oil obtained from mustard seed belongs to this class of compounds—

HSCN	$\begin{array}{l} CH_3 \\ \vert \\ S\cdot C\vdots N \end{array}$	$\begin{array}{l} CH_3 \\ \vert \\ N\colon C\colon S \end{array}$
Thiocyanic acid.	Methyl thiocyanate.	Methyl isothiocyanate, or Methyl mustard oil.

Attention is called to the fact that all the iso-esters contain the carbon of *the alkyl group linked to nitrogen.*

The Alkyl Cyanides or **Nitriles.**—Certain methods of preparation of the cyanides have already been described. The alkyl cyanides may be obtained by the action of potassium cyanide in aqueous alcoholic solution upon the alkyl iodide (p. 84)—

$$CH_3I + KCN = CH_3CN + KI,$$

or by distilling the amides with phosphorus pentoxide (p. 180).

Acetamide is converted in this way into methyl cyanide—

$$CH_3\cdot CO\cdot NH_2 - H_2O = CH_3CN.$$

EXPT. 86. *Preparation of Methyl Cyanide or Acetonitrile.*—Mix together 10 grams of dry acetamide and 15 grams of phosphorus pentoxide in a small retort or distilling flask attached to a condenser and receiver. Heat the mixture over a small flame. Collect the liquid which distils, and add a few c.c. of water and then solid potassium carbonate until no more dissolves. The upper layer of liquid is removed and redistilled over fresh phosphorus pentoxide. Methyl cyanide boils at 82°.

The lower members of the series are colourless liquids with a strong but not unpleasant smell. They are soluble to some extent in water. The higher members are less soluble in water, and are solid crystalline substances.

The most important characteristics of the alkyl cyanides are their rapid conversion into fatty acids on hydrolysis with mineral acids or alkalis, and their reduction to the corresponding amine by the action of sodium on the alcoholic solution of the cyanide. Methyl cyanide is converted into ethylamine in the same way that hydrocyanic acid is reduced to methylamine (p. 213)—

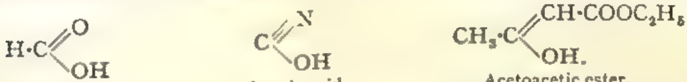
$$CH_3C\vdots N + 2H_2 = \underset{\text{Ethylamine.}}{CH_3{\cdot}CH_2{\cdot}NH_2}.$$

The formation of acids and amines from the cyanides clearly indicates that the carbon of the cyanogen group is directly linked to the carbon of the alkyl group.

Unsaturated Groups.—The many reactions into which the alkyl cyanides enter cannot be discussed here in detail. They resemble the aldehydes and ketones in the variety of derivatives to which they give rise. The resemblance is without doubt connected with the ketone group, $C{:}O$, in the one case, and the cyanogen group, $C\vdots N$, in the other. In both groups carbon is represented as linked to a second element by more than one bond. The groups are termed *unsaturated* because they are capable of taking up additional atoms. They readily unite with hydrogen: the aldehydes and ketones form alcohols in this manner; the cyanides yield primary amines. The elements of water, alcohol, hydrogen sulphide, the halogen acids, hydroxylamine, and the halogens all readily combine with the alkyl cyanides, and form additive compounds in much the same way that hydrocyanic acid, sodium bisulphite, and ammonia combine with aldehydes (p. 131). A multiple linkage, similar to that which exists in the groups $C{:}O$ and $C\vdots N$, is found to occur between two carbon atoms in the compounds known as unsaturated hydrocarbons and their derivatives, which are described in Chap. XVII, p. 246. A further resemblance may be pointed out.

The presence of these groups gives to the organic compound in which they occur a more strongly acid character. Reference to this point will be again brought forward (p. 347).

For the present it is only necessary to mention the acid character of the fatty acids, cyanic acid, and acetoacetic ester. In all these examples the hydrogen of the hydroxyl group is replaceable by a metal—



Formic acid. Cyanic acid. Acetoacetic ester. (Alternative formula, p. 328.)

The Alkyl Isocyanides, or **Carbamines,** or **Isonitriles** are isomeric with the cyanides. They are formed by the action of chloroform and alcoholic potash on the primary amines (p. 203).

Methyl isocyanide is prepared by distilling a mixture of methylamine, chloroform, and alcoholic potash—

$$CH_3N\boxed{H_2 + C}HCl_3 + 3KOH = \underset{\text{Methyl isocyanide.}}{CH_3NC} + 3KCl + 3H_2O.$$

The isocyanides are also obtained by distilling a mixture of alkyl iodide and silver cyanide—

$$CH_3\boxed{I + Ag}NC = \underset{\text{Methyl isocyanide.}}{CH_3NC} + AgI.$$

It would appear from this reaction that silver cyanide is differently constituted from the potassium salt, which gives under similar conditions the normal cyanide (p. 225); or, it may be that the higher temperature required to effect the decomposition in the case of the silver compound may produce the change of structure. It is noteworthy that although the amount of cyanide greatly predominates, some isocyanide is always formed when a mixture of alkyl potassium sulphate and potassium cyanide is distilled—

$$CH_3\boxed{O{\cdot}SO_3K + K}CN = \underset{\text{Methyl cyanide, and isocyanide.}}{\begin{cases} CH_3CN \\ CH_3NC \end{cases}} + K_2SO_4.$$

This fact would indicate that other conditions than the structure of the metallic cyanide, determine the formation of one or the other isomer. It is generally agreed that the metallic cyanides are isocyanides, whilst hydrocyanic acid is regarded as a nitrile, though the evidence is not conclusive.

The isocyanides are liquids with an intolerable smell. The boiling-points are lower than those of the corresponding cyanides. They are hydrolysed by hydrochloric acid into amines and formic acid, the reaction probably occurring in two steps.

In the first, the alkyl formamide is produced, which then decomposes into amine and formic acid—

$$1.\ CH_3NC + H_2O = \underset{\text{Methyl formamide.}}{CH_3NH{\cdot}CHO.}$$

$$2.\ CH_3NH{\cdot}CHO + H_2O = \underset{\text{Methylamine.}}{CH_3NH_2} + \underset{\text{Formic acid.}}{HCO{\cdot}OH.}$$

Unlike the cyanides the isocyanides are not decomposed when boiled with alkalis. They can however be reduced to secondary amines by heating with hydrogen in the presence of a nickel catalyst.

$$CH_3{\cdot}NC + 2H_2 = CH_3{\cdot}NH{\cdot}CH_3$$

Both the mode of formation from, and conversion into the primary amine indicate that in the alkyl isocyanides, nitrogen is directly united to carbon of the alkyl group (p. 213).

The Alkyl Cyanates and Isocyanates (Carbimides).—The alkyl cyanates are prepared by acting on cyanogen chloride with sodium alcoholate. Methyl alcoholate gives methyl cyanate—

$$CN\boxed{Cl + Na}OCH_3 = \underset{\text{Methyl cyanate.}}{NC{\cdot}OCH_3.}$$

They are colourless ethereal smelling liquids, which have not yet been obtained in the pure state; for they rapidly polymerise and pass into alkyl cyanurates (see next page).

The isocyanic esters are much more readily obtained. They were originally prepared by Wurtz (1854) by distilling an alkyl potassium sulphate with potassium cyanate—

$$\underset{\substack{\text{Potassium methyl}\\ \text{sulphate.}}}{CH_3\boxed{OSO_3K + K}}NCO = \underset{\substack{\text{Methyl}\\ \text{isocyanate.}}}{CH_3N{:}CO} + K_2SO_4.$$

A more convenient method is to heat a mixture of silver cyanate and alkyl iodide—

$$CH_3\boxed{I + Ag}NCO = CH_3N{:}CO + AgI.$$

Another method is to warm the acyl azoimide (obtained from

the acyl chloride and sodium azoimide) which loses nitrogen, thus—

$$CH_3CO{\cdot}N_3 \longrightarrow CH_3N{:}CO + N_2.$$

Acetyl azoimide gives methyl isocyanate.

The isocyanic esters are volatile liquids with a powerful and suffocating odour. Like the cyanic esters they polymerise on standing, forming isocyanuric esters. The most interesting property of the isocyanic esters is their conversion into amines on boiling with alkalis (p. 200)—

$$\underset{\text{Methyl isocyanate.}}{CH_3N{:}CO} + H_2O = \underset{\text{Methylamine.}}{CH_3NH_2} + CO_2.$$

They also unite with amino- and hydroxyl groups and are used as reagents for these groups, thus—

$$R{\cdot}OH + CH_3N{:}CO = RO{\cdot}CO{\cdot}NHCH_3$$
$$R{\cdot}NH_2 + CH_3N{:}CO = R{\cdot}NH{\cdot}CO{\cdot}NHCH_3.$$

In the first case a substance known as a urethane is obtained (p. 337) and in the second a derivative of urea.

The Alkyl Cyanurates and Isocyanurates are formed by the polymerisation of the corresponding cyanates and isocyanates. The alkyl cyanurates are also obtained by acting upon cyanuric chloride with sodium alcoholate—

$$C_3N_3Cl_3 + 3NaOCH_3 = \underset{\text{Methyl cyanurate.}}{N_3C_3(OCH_3)_3} + 3NaCl.$$

The Alkyl Thiocyanates and Isothiocyanates.—The thiocyanates are obtained by the action of an alkyl iodide on potassium thiocyanate. Methyl iodide gives methyl thiocyanate—

$$CNS\boxed{K + I}CH_3 = \underset{\text{Methyl thiocyanate.}}{CNSCH_3} + KI.$$

The structure of the thiocyanates is determined by their reduction to mercaptan and amine—

$$CH_3SCN + 3H_2 = CH_3SH + CH_3NH_2,$$

and by their oxidation to sulphonic acids—

$$CH_3S{\cdot}CN \longrightarrow CH_3{\cdot}SO_3H.$$

On prolonged heating the alkyl thiocyanates are converted into the isomeric isothiocyanates.

The Mustard Oils, or *Alkyl isothiocyanates*, are most easily obtained by the action of carbon bisulphide on the primary amines. The method is analogous to the formation of ammonium thiocyanate (p. 223). The compound first formed is the alkylamine salt of an alkyl thiocarbamate—

$$CS_2 + 2NH_2CH_3 = CS\left\langle\begin{array}{l}NHCH_3\\ SH\cdot NH_2\cdot CH_3.\end{array}\right.$$

Methylamine methyl thiocarbamate.

If this compound is now treated with mercuric chloride, hydrogen sulphide is removed, and the thiocarbamate splits up into the mustard oil and primary amine—

$$SC\left\langle\begin{array}{l}N\boxed{H}CH_3\\ \boxed{SH}\ NH_2\cdot CH_3\end{array}\right. = SC\colon NCH_3 + NH_2\cdot CH_3 + H_2S.$$

Methyl mustard oil.

The above reaction is occasionally used as a test for primary amines (p. 202).

Questions on Chapter XV

1. How is cyanogen most easily prepared? Compare cyanogen and chlorine.

2. What products are obtained by the hydrolysis of cyanogen, hydrocyanic acid, methyl cyanide, methyl isocyanide, and methyl isocyanate? What reagent is required in each case?

3. Describe a method for preparing potassium cyanide and sodium cyanide. In what manner has atmospheric nitrogen been utilised in the preparation of cyanides?

4. How is hydrocyanic acid detected? Describe a quantitative method for analysing potassium cyanide.

5. What is meant by a *double cyanide?* How may the two classes of double cyanides be distinguished?

6. How is yellow prussiate of potash converted into the red prussiate, and *vice versa?*

7. Describe and explain the formation of urea from potassium cyanide.

8. How may the following compounds be obtained from potassium ferrocyanide: carbon monoxide, hydrocyanic acid, potassium cyanide, hydroferrocyanic acid, and cyanogen?

9. What is meant by the term *mustard oil?* How are the mustard oils obtained?

10. Discuss the structure of isomeric compounds of the formula C_3H_5N (cyanide and isocyanide).

11. Explain the meaning of the term *unsaturated group*. Illustrate your answer by reference to acetaldehyde and methyl cyanide.

12. Discuss the structure of hydrocyanic acid and the metallic cyanides.

13. Give an account of the preparation and properties of cyanogen gas. Why is cyanogen considered to be analogous to chlorine, and in what respects does it differ from chlorine?

14. How is potassium ferrocyanide manufactured? How would you prepare from potassium ferrocyanide (*a*) a dilute solution of prussic acid, (*b*) urea, (*c*) carbon monoxide?

15. How do you account for the different action of strong and dilute sulphuric acid on potassium ferrocyanide?

16. Starting from mercury and potassium ferrocyanide, how would you prepare mercuric cyanide? Describe its properties, and compare them with those of potassium cyanide.

17. Describe the mode of preparation and properties of cyanic and cyanuric acids. Point out the relation between the two substances.

18. Explain by examples the isomerism of carbamines and nitriles. How is each class of bodies prepared? How can the formulæ ascribed to each be proved to be correct?

19. What is a nitrile? How can it be obtained from an ammonium salt, and what transformation does it undergo when hydrolysed and when reduced by nascent hydrogen?

CHAPTER XVI

THE ALKYL COMPOUNDS OF PHOSPHORUS, ARSENIC, AND SILICON, AND THE ORGANO-METALLIC COMPOUNDS

The Phosphines.—The alkyl compounds of phosphorus, which correspond in composition to the amines (p. 200), are known as *phosphines*. They may be regarded as derivatives of ordinary phosphine or hydrogen phosphide, PH_3. The methyl derivatives have the following formulæ—

PH_3	CH_3PH_2	$(CH_3)_2PH$	$(CH_3)_3P$
Phosphine.	Methyl phosphine, b.p. $-14°$.	Dimethyl phosphine, b.p. 25°.	Trimethyl phosphine, b.p. 40°–42°.

Quaternary phosphonium compounds—iodides and hydroxides—are also known—

$(CH_3)_4PI$	$(CH_3)_4P{\cdot}OH.$
Tetramethyl phosphonium iodide.	Tetramethyl phosphonium hydroxide.

By the action of an alkyl iodide on phosphine, PH_3, only tertiary alkyl phosphines are formed. In order to obtain the primary and secondary compounds, the alkyl iodide is heated with phosphonium iodide in the presence of zinc oxide. Mono- and di-methyl phosphine are formed according to the following equations—

$$2CH_3I + 2PH_4I + ZnO = \underset{\text{Methyl phosphine hydriodide.}}{2CH_3{\cdot}PH_2{\cdot}HI} + ZnI_2 + H_2O.$$

$$2CH_3I + PH_4I + ZnO = \underset{\text{Dimethyl phosphine hydriodide.}}{(CH_3)_2PH{\cdot}HI} + ZnI_2 + H_2O.$$

The tertiary phosphines are most conveniently prepared by the action of the alcohol on phosphonium iodide in sealed tubes. The phosphonium iodide and alcohol are converted into alkyl iodide and phosphine, which then react upon one another. Methyl alcohol and phosphonium iodide give trimethyl phosphine hydriodide—

$$CH_3OH + PH_4I = PH_3 + CH_3I + H_2O.$$

$$3CH_3I + PH_3 = \underset{\text{Trimethyl phosphine hydriodide.}}{(CH_3)_3P{\cdot}HI} + 2HI.$$

Properties of Phosphines.—The phosphines are colourless liquids (with the exception of mono-methyl phosphine, which is a gas) with a penetrating and unpleasant smell. Even the lower members are only slightly soluble in water. The phosphines are much less basic than the corresponding amines; for, though they combine with acids and form soluble salts, having a similar composition to those of the amines, the phosphines themselves are not alkaline, and the salts of the primary phosphines are decomposed like phosphonium iodide, by water, into the phosphine and acid.

The quaternary iodides and hydroxides are prepared in the same manner as the ammonium compounds; the phosphonium hydroxides, like the ammonium hydroxides, dissolve readily in water, forming strongly alkaline solutions, which absorb carbon dioxide from the air and neutralise acids.

The phosphines readily undergo oxidation, the phosphorus becoming quinquevalent by uniting with an atom of oxygen, in addition to which the hydrogen in the primary and secondary phosphines is replaced by hydroxyl. Thus, the primary and secondary phosphines are converted into **phosphinic acids.** The following products are obtained by the action of nitric acid on the three methyl phosphines—

$$\left.\begin{array}{l} CH_3 \\ HO \\ HO \end{array}\right> PO \qquad \left.\begin{array}{l} CH_3 \\ CH_3 \\ HO \end{array}\right> PO \qquad \left.\begin{array}{l} CH_3 \\ CH_3 \\ CH_3 \end{array}\right> PO$$

Methyl phosphinic acid. | Dimethyl phosphinic acid. | Trimethyl phosphonium oxide.

The tendency to undergo oxidation exhibited by the phosphines (it has been observed in a few tertiary amines under the influence of a powerful oxidising agent, *e.g.* hydrogen peroxide) is much more marked in the case of the alkyl compounds of the more metallic elements, many of which oxidise in the air.

The Arsines.—The primary, secondary, and tertiary arsines are known. The corresponding chlorine derivatives have also been obtained. The methyl compounds have the following formulæ—

$$\left.\begin{array}{l} CH_3 \\ Cl \\ Cl \end{array}\right> As. \qquad\qquad \left.\begin{array}{l} CH_3 \\ CH_3 \\ Cl \end{array}\right> As.$$

Methyl arsine chloride. | Dimethyl arsine chloride, or Cacodyl chloride.

The tertiary arsines, and the quaternary arsonium iodides and hydroxides, have the following formulæ—

$(CH_3)_3As$	$(CH_3)_4As{\cdot}I$	$(CH_3)_4As{\cdot}OH$.
Trimethyl arsine. b.p. 70°.	Tetramethyl arsonium iodide.	Tetramethyl arsonium hydroxide.

The quaternary iodides and hydroxides are obtained by the method employed in the case of the amines and phosphines. The arsonium hydroxides resemble the ammonium and phosphonium compounds. They are freely soluble in water, have an alkaline reaction, and neutralise acids.

The tertiary arsines are obtained when a zinc alkyl (p. 238) acts upon arsenic trichloride or when an alkyl iodide is heated with sodium arsenide. The formation of the methyl compounds is represented by the following equations—

$$1.\quad 2AsCl_3 + \underset{\text{Zinc methyl.}}{3Zn(CH_3)_2} = \underset{\text{Trimethyl arsine.}}{2As(CH_3)_3} + 3ZnCl_2.$$

$$2.\quad AsNa_3 + 3CH_3I = As(CH_3)_3 + 3NaI.$$

The tertiary arsines are without basic properties and form no salts. They readily combine with the halogens and sulphur, and take up the oxygen from the air, the arsenic thereby becoming pentavalent. Trimethylarsine forms the following well-defined compounds—

$(CH_3)_3AsCl_2$.	$(CH_3)_3AsS$.	$(CH_3)_3AsO$.
Trimethyl arsine dichloride.	Trimethyl arsine sulphide.	Trimethyl arsine oxide.

Cacodyl Compounds.—When a mixture of equal parts of potassium acetate and arsenious oxide is heated, a liquid distils which has an intolerable smell, is spontaneously inflammable, and excessively poisonous. It was first obtained by Cadet in 1760, and was known as "Cadet's fuming liquid." The composition of this substance was ascertained by Bunsen (1837–1843), who named it *cacodyl oxide* (κακώδης, stinking) from its smell. Bunsen showed that it was the oxide of the radical **cacodyl,** AsC_2H_6 [afterwards changed to $As(CH_3)_2$]. Like the radical cyanogen,—CN, which plays the part of a halogen or monovalent acid radical, so cacodyl plays the part of a univalent metal, and may be termed a basic radical. Thus, cacodyl chloride, $As(CH_3)_2Cl$, platinochloride, $[As(CH_3)_2Cl]_2PtCl_4$,

and cyanide, $As(CH_3)_2CN$, etc., are known. The reaction by which cacodyl oxide is formed is expressed by the following equation—

$$As_2O_3 + 4CH_3{\cdot}COOK = O\begin{matrix} \diagup As(CH_3)_2 \\ \diagdown As(CH_3)_2 \end{matrix} + 2K_2CO_3 + 2CO_2.$$

Cacodyl oxide.

The reaction is used as a delicate test for arsenic or acetic acid, a small quantity of either substance under appropriate conditions giving the characteristic smell, which is easily recognised.

When cacodyl oxide is exposed to the air or heated with mercuric oxide, it takes up oxygen and water and is converted into **cacodylic acid**—

$$\begin{matrix} (CH_3)_2As\diagdown \\ (CH_3)_2As\diagup \end{matrix}O + O_2 + H_2O = 2(CH_3)_2As\begin{matrix} \diagup\!\!\diagup O \\ \diagdown OH. \end{matrix}$$

Cacodylic acid.

Cacodylic acid is a crystalline substance, forming salts which are for the most part insoluble in water and non-poisonous. Some of the salts have been introduced into medicine.

When cacodyl oxide is distilled with hydrochloric acid, *cacodyl chloride* is formed. The reaction resembles the formation of sodium chloride from the oxide—

$$\begin{matrix} (CH_3)_2As\diagdown \\ (CH_3)_2As\diagup \end{matrix}O + 2HCl = 2(CH_3)_2AsCl + H_2O.$$

Cacodyl chloride.

$$\begin{matrix} Na\diagdown \\ Na\diagup \end{matrix}O + 2HCl = 2NaCl + H_2O.$$

The chloride may be reconverted into the oxide by caustic alkalis, a reaction which again resembles the behaviour of certain metallic chlorides.

When cacodyl chloride is treated with metallic zinc in an atmosphere of carbon dioxide, **cacodyl**, or more correctly dicacodyl (tetramethyl diarsine), is formed—

$$\begin{matrix} As(CH_3)_2\,|\,Cl \\ As(CH_3)_2\,|\,Cl \end{matrix} + Zn = \begin{matrix} As(CH_3)_2 \\ | \\ As(CH_3)_2 \end{matrix} + ZnCl_2.$$

Cacodyl.

Cacodyl is a colourless, mobile, and highly refractive liquid, which oxidises so rapidly in the air that it inflames spontaneously, giving off carbon dioxide and water and fumes of arsenic trioxide.

Some of the organic derivatives of arsenic have been used in warfare as so-called poison gases. *Lewisite*, the deadly vesicant liquid with a smell of geraniums, is 2-chlorovinyl dichloroarsine $CHCl{:}CHAsCl_2$. Some other arsenical compounds form irritant, poisonous smokes.

Alkaline Alkyl Compounds.—The frequent appearance among organic compounds of derivatives of the most diverse elements possessing marked alkaline characters is very striking. Elements belonging to entirely different groups of the periodic system, such as iodine, mercury, sulphur, and nitrogen (phosphorus or arsenic), form compounds which have properties like ammonia. In these compounds, the alkaline character is associated with the presence of hydrogen (in ammonia) alkyl groups, or other hydrocarbon radicals, linked along with hydroxyl to a polyvalent element, the valency of which is, more or less, *saturated*. The following examples will make these points clear—

$(C_6H_5)_2I{\cdot}OH$	$(C_2H_5)Hg{\cdot}OH$	$(CH_3)_3S{\cdot}OH$	$(CH_3)_4\begin{pmatrix}N\\P\\As\end{pmatrix}OH.$
Diphenyl-iodonium hydroxide.	Ethyl mercury hydroxide.	Trimethyl sulphinium hydroxide.	Tetramethyl ammonium, etc., hydroxide.

The above series of compounds possesses the same general properties. They dissolve in water, forming strongly alkaline solutions, which can be neutralised by acids and precipitate metallic oxides from their salts. Recently, a compound, trianisyl carbinol, or carbonium hydroxide, $(CH_3O{\cdot}C_6H_4)_3C{\cdot}OH$, has been prepared, which has basic properties, and forms well-defined salts.

It is interesting to compare these basic compounds with the organic acids, which are also characterised by the presence of a hydroxyl group. The hydroxyl group of acids is usually associated with *unsaturated* groups, as in carboxyl, $-COOH$, and the sulphonic acid group $-SO_2OH$.

Silicon Alkyl Compounds.—Silicon, like carbon, is quadrivalent, and stands nearest to carbon in the periodic system. The alkyl compounds of silicon have in consequence a special interest from the analogy which they might be expected to offer with the paraffins. Silicon tetramethyl, or silico-pentane, $Si(CH_3)_4$, corresponds to neopentane, or tetramethyl methane, $C(CH_3)_4$ (p. 75); silicon tetraethyl, or silico-nonane, $Si(C_2H_5)_4$, corresponds to tetraethyl methane, $C(C_2H_5)_4$. Silicon tetramethyl is obtained from silicon

chloride and zinc methyl, or by Grignard's method with magnesium methyl bromide (see p. 243).

$$SiCl_4 + 2Zn(CH_3)_2 = \underset{\text{Silicon tetramethyl.}}{Si(CH_3)_4} + 2ZnCl_2$$

Silicon tetraethyl is prepared in the same manner from zinc ethyl. Like the paraffins, the silicon alkyls are colourless liquids, specifically lighter than water, in which they are insoluble. They are unattacked by strong sulphuric or strong nitric acids. The boiling-points compared with those of the paraffins are as follows:—

Silico-pentane . .	30°–31°	norm. pentane . . neo-pentane . .	37° 9°
Silico-nonane . .	151°–153°	norm. nonane . .	150°

Silico-nonane, when chlorinated, forms a chlorine substitution product, $SiC_8H_{19}Cl$, which is a colourless liquid boiling at 185°. The chlorine may be exchanged for hydroxyl, when silico-nonyl alcohol, $SiC_8H_{19}\cdot OH$, is produced, possessing many of the properties of an alcohol.

By combining silicon with four different radicals, compounds have been prepared containing an *asymmetric* silicon atom (p. 115), which like active amyl alcohol, exhibits optical activity (Kipping).

Organo-metallic Compounds.—The term is applied to the alkyl compounds of the metals. They resemble certain of the alkyl compounds of the non-metals, both in their mode of preparation and properties. In fact, no sharp line can be drawn between the two. There is the same gradual transition which characterises the change from non-metals to metals.

In this connection we may compare the alkyl with the hydrogen compounds of the elements. Thus, we find that, as the metallic character of an element predominates, its affinity for hydrogen diminishes. If such metallic hydrides exist, they are very unstable, and, on heating, lose hydrogen. In the same way the alkyl compounds of the metals are much less stable than those of the non-metals. They unite with oxygen with great avidity, frequently taking fire in the air, and decompose water, alcohol, and other organic compounds containing oxygen. The number of organo-metallic compounds is very large, and for our present purpose a study of the zinc and magnesium compounds must suffice.

Zinc Alkyl Compounds.—The study of the zinc alkyl compounds is closely linked with the history of organic chemistry. It was with the object of isolating the organic radicals by removing iodine from the alkyl iodides that Frankland discovered the twofold action of zinc on the alkyl iodides (1849). Frankland's radicals proved to be paraffins, and an important synthetic method was thereby introduced, which has already been described (p. 72). Methyl iodide and metallic zinc yield ethane—

$$2CH_3I + Zn = C_2H_6 + ZnI_2.$$

If an excess of zinc is used, zinc alkyl compounds are formed. The process actually occurs in two steps. When metallic zinc or the zinc-copper couple (p. 82) is boiled with an alkyl iodide, zinc alkyl iodide is formed—

$$CH_3I + Zn = \underset{\text{Zinc methyl iodide.}}{Zn\langle^{CH_3}_{I}}$$

When the product of the first reaction is distilled, it is decomposed into zinc alkyl and zinc iodide—

$$2Zn\langle^{CH_3}_{I} = \underset{\text{Zinc methyl.}}{Zn(CH_3)_2} + ZnI_2.$$

EXPT. 87. *Preparation of Zinc Ethyl.*—A round distilling flask, the side-tube of which is temporarily closed, is attached to an inverted condenser. Through a cork in the upper end of the condenser a bent tube is tightly inserted, the lower end of which dips into mercury. The object of this arrangement is to prevent the entrance of air, in which the zinc ethyl readily takes fire. Equal weights of zinc-copper couple (60 grams) and ethyl iodide (60 grams) are placed in the flask attached to the condenser. The zinc-copper couple is made by mixing zinc dust (50 grams) with fine copper oxide powder (10 grams), previously reduced in a current of hydrogen. The mixture in the flask is heated on the water-bath until the evolution of gas (butane), which occurs at the beginning, ceases (about 2 hours). The first reaction is then at an end, and the liquid is next distilled in an oil- or metal-bath in a current of dry carbon dioxide. A small flask is used as the receiver. The liquid, which passes over, is zinc ethyl, boiling at 118°. The zinc ethyl is now introduced into small bulbs for subsequent experiments. These bulbs have a capacity of 2–3 c.c., and are made with long narrow

stems, or tubes, bent at right angles, and open at the end. The bulbs, filled with coal gas by placing them in a desiccator exhausting and allowing coal gas to enter, are placed with the open ends downwards in the flask containing the zinc ethyl, as shown in Fig. 65. The flask is quickly placed in a vacuum desiccator filled with coal-gas, which is then exhausted. On allowing coal-gas to enter, the liquid enters the bulbs, which are removed and sealed.

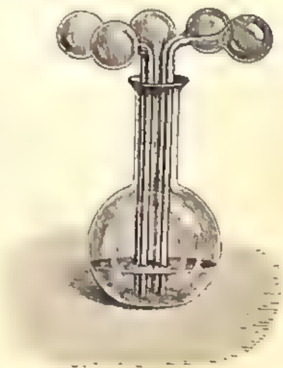


FIG. 65.—Method of filling bulbs with Zinc ethyl.

When exposed to the air, the zinc alkyl rapidly oxidises, and the heat developed is sufficient to inflame the substance, which burns with a white luminous flame, evolving carbon dioxide and water together with fumes of zinc oxide.

EXPT. 88.—Break off the end of the stem of one of the bulbs of zinc ethyl prepared in Expt. 87 and shake out the contents. The liquid takes fire on coming in contact with the air.

A similar change happens when the halogens act upon a zinc alkyl compound. The substance takes fire, and the metallic halide is formed. If the reaction is moderated by dissolving the reacting substances in an inert solvent, zinc halide and alkyl halide are formed. Zinc methyl and iodine form zinc iodide and methyl iodide—

$$Zn(CH_3)_2 + 2I_2 = ZnI_2 + 2CH_3I.$$

SYNTHETIC PROCESSES IN WHICH THE ZINC ALKYL COMPOUNDS ARE USED

Synthesis of Organo-metallic Compounds.—The preparation of arsenic and silicon alkyl compounds by means of zinc alkyls has already been described (pp. 234, 236). Alkyl compounds of different metals have been obtained in the same way by the action of a zinc alkyl on the chlorides of antimony, bismuth, tin, lead, mercury, etc. The following methyl compounds of these metals have been obtained. They are liquids which can be vaporised

unchanged, so that their molecular weights have been correctly ascertained.

$$\begin{array}{ll} Hg(CH_3)_2 & Sn(CH_3)_4 \\ Bi(CH_3)_3 & Pb(CH_3)_4 \\ Sb(CH_3)_3 & \end{array}$$

In comparing the alkyl compounds with the non-metallic compounds of the elements, Frankland was struck with the correspondence in what he called "saturation capacity," or, as we now term it, the "valency" of the elements, and he was the first to draw attention to this property, which has exercised so important an influence on chemical theory.

Synthesis of the Paraffins.—When the zinc alkyl comes in contact with water, the water is decomposed, the hydrogen attaching itself to the alkyl group and forming a paraffin, whilst the oxygen combines with the zinc. Zinc methyl gives zinc hydroxide and methane—

$$Zn\left\langle \begin{array}{ccc} CH_3 & & H \\ & + & \\ CH_3 & & H \end{array} \right. O + H_2O = Zn(OH)_2 + 2CH_4.$$

EXPT. 89.—By means of pliers take one of the bulbs of zinc ethyl (Expt. 87) by the long stem and introduce it below an inverted cylinder or gas-jar filled with water. Break the stem between the pliers. A copious evolution of gas follows and partly fills the cylinder, whilst at the same time a bulky white precipitate of zinc hydroxide is deposited. By closing the mouth, the cylinder may be brought into an upright position and the gas ignited by a taper. Zinc ethyl yields ethane.

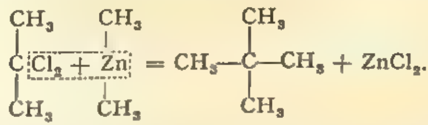
The synthesis of the paraffins may be simplified by heating together in a sealed vessel a mixture of zinc, alkyl iodide, and water. Probably the zinc alkyl is formed as an intermediate product, which is decomposed in the presence of water. Methyl iodide yields methane by this method—

$$2CH_3I + Zn_2 + 2H_2O = 2CH_4 + ZnI_2 + Zn(OH)_2.$$

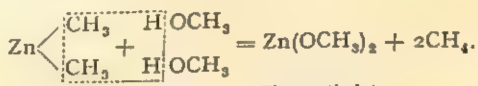
A further synthesis of the paraffins is effected by the action of the alkyl iodides on the zinc alkyl; zinc methyl and methyl iodide give ethane—

$$Zn \begin{array}{ccc} CH_3 & & CH_3 \\ & + & \\ CH_3 & & CH_3 \end{array} \begin{array}{c} I \\ \\ I \end{array} = ZnI_2 + 2C_2H_6.$$

By a similar reaction neo-paraffins may be obtained. ββ-Dichloropropane and zinc methyl give neo-pentane (p. 75)—

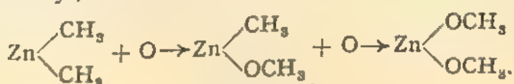


A very similar reaction to that produced by adding water to the zinc alkyl occurs when the latter is decomposed by alcohol. Zinc alcoholate is thereby formed, and the alkyl group takes up hydrogen and forms a paraffin. Zinc methyl and methyl alcohol yield methane and zinc methylate—



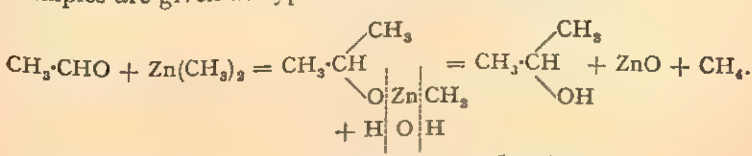
Zinc methyl. Methyl alcohol. Zinc methylate or methoxide.

The same product is obtained by the gradual absorption of oxygen by the zinc alkyl, the reaction actually occurring in two steps—



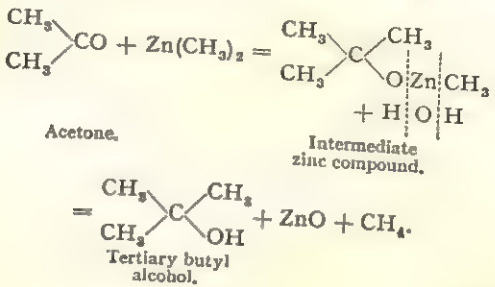
Zinc methyl. methoxide.

Synthesis of Secondary and Tertiary Alcohols and Ketones.—From what has been already explained of the affinity exhibited by the zinc alkyl compounds for oxygen and the halogens, the following reactions will be readily understood. In reactions with aldehydes and ketones to be described, the zinc atom attaches itself to the oxygen atom of the unsaturated group, CO, by one bond, losing at the same time an alkyl group, which is transferred to the unsaturated carbon atom of the same group. This represents the first stage in the reaction. The product is subsequently decomposed with water, by which the alcohol is produced. The following examples are given as typical of this class of reactions—



Acetaldehyde. Intermediate zinc compound. Secondary propyl alcohol.

Acetaldehyde and zinc methyl yield secondary propyl alcohol. In the same way acetone and zinc methyl form tertiary butyl alcohol—



Acetone. Intermediate zinc compound. Tertiary butyl alcohol.

Magnesium alkyl halides.—The discovery by Grignard of the magnesium alkyl halides has rendered the use of the zinc compounds unnecessary, and at the same time has provided an extremely valuable weapon with which to attack constitutional problems which involve complex syntheses. The so-called Grignard reagents are readily prepared in open flasks in the form of ethereal solutions, from which they need not be isolated, and they give the same sort of reactions as the much more troublesome zinc alkyls. For their preparation only the purest materials should be used, and care should be taken to exclude traces of moisture. The ether is kept dry with sodium, and pure magnesium turnings are preferable to the powder. When an alkyl halide is brought into contact with magnesium in the presence of dry ether, the magnesium dissolves and a magnesium alkyl halide is formed. Thus methyl iodide gives methyl magnesium iodide, $CH_3 \cdot Mg \cdot I$. The reaction does not take place unless ether is present, and if the excess of ether be distilled off, a glassy residue remains, which is found to consist of the magnesium alkyl halide combined with ether. The exact constitution of this compound is not certain, but it is generally assumed that the oxygen atom of the ether is co-ordinated (Chapter XXIV) to the magnesium. In considering the reactions of the Grignard reagents, we may ignore the ether, except as a solvent. It is not usually included in the equations.

These substances are decomposed by water, forming paraffins—

$$CH_3 \cdot MgBr + H_2O = CH_4 + MgBr(OH).$$

They also combine with non-metallic and metallic chlorides to form alkyl derivatives. Silicon methyl can be prepared in this way by a repetition of the following process:

$$SiCl_4 + CH_3MgBr = SiCl_3CH_3 + MgClBr.$$

The magnesium alkyl halides combine with aldehydes, ketones, esters, and acid chlorides after the manner of the zinc alkyls, and the products when decomposed with water form secondary and tertiary alcohols and ketones. Thus, for example, acetaldehyde and magnesium methyl iodide yield secondary propyl alcohol—

$$CH_3{\cdot}CHO + \underset{\text{Methyl magnesium iodide.}}{CH_3MgI} = \underset{\text{Intermediate magnesium compound.}}{CH_3{\cdot}CH\begin{matrix}\diagup CH_3 \\ \diagdown O\,|\,Mg\,|\,I \\ \quad + \\ \quad H\,|\,O\,|\,H\end{matrix}}$$

$$= \underset{\text{Secondary propyl alcohol.}}{CH_3{\cdot}CH\begin{matrix}\diagup CH_3 \\ \diagdown OH\end{matrix}} + \underset{\text{Magnesium oxyiodide.}}{Mg\begin{matrix}\diagup I \\ \diagdown OH.\end{matrix}}$$

Primary alcohols can be obtained from formaldehyde, whereas ketones and esters yield tertiary alcohols—

$$(CH_3)_2CO + CH_3MgI \longrightarrow$$

$$(CH_3)_2C\begin{matrix}\diagup CH_3 \\ \diagdown OMgI\end{matrix} \longrightarrow (CH_3)_2C(OH)CH_3.$$

Expt. 90.—Add 3 grams of clean magnesium ribbon or filings to 75 c.c. of perfectly dry ether and then pour in 18 grams of methyl iodide, the flask being attached to a reflux condenser. The magnesium rapidly dissolves. Cool and add to the solution 7 grams of acetone. A white, bulky precipitate of the magnesium compound is deposited. On dissolving in dilute sulphuric acid, the ether solution of the alcohol separates, and may be withdrawn and distilled.

The carbonyl group of an ester reacts as usual, but the alkyloxy-group also takes part, being replaced by alkyl, thus forming a tertiary alcohol—

$$CH_3\cdot C\begin{array}{l}\diagup\!\!\!\diagup O\\ \diagdown O\cdot C_2H_5\end{array} + CH_3MgI = CH_3\cdot C\begin{array}{l}\diagup OMgI\\ -CH_3\\ \diagdown OC_2H_5\end{array}$$

$$CH_3\cdot C\begin{array}{l}\diagup OMgI\\ -CH_3\\ \diagdown OC_2H_5\end{array} + CH_3MgI = CH_3\cdot C\begin{array}{l}\diagup OMgI\\ -CH_3\\ \diagdown CH_3\end{array} + Mg\begin{array}{l}\diagup I\\ \diagdown OC_2H_5\end{array}$$

$$CH_3\cdot C\begin{array}{l}\diagup OMgI\\ -CH_3\\ \diagdown CH_3\end{array} + H_2O \quad = (CH_3)_3C\cdot OH + MgI(OH).$$

Ketones can be prepared from cyanides and amides :

$$CH_3CN + C_2H_5MgBr \longrightarrow$$

$$CH_3\cdot C\begin{array}{l}\diagup\!\!\!\diagup NMgBr\\ \diagdown C_2H_5\end{array} \xrightarrow{H_2O} \begin{array}{l}CH_3COC_2H_5 +\\ Mg(OH)Br + NH_3.\end{array}$$

$$CH_3CONH_2 + 2C_2H_5MgI = CH_3\cdot C\begin{array}{l}\diagup NHMgI\\ -OMgI\\ \diagdown C_2H_5\end{array} + C_2H_6 \longrightarrow$$

$$CH_3\cdot CO\cdot C_2H_5 + MgI_2 + Mg(OH)_2 + NH_3.$$

The magnesium alkyl halides absorb carbon dioxide, and form thereby compounds, which are decomposed by alkalis and yield salts of the fatty acids. Methyl bromide gives acetic, ethyl bromide forms propionic acid—

$$C_2H_5MgBr + CO_2 = C_2H_5CO\cdot OMgBr.$$
$$C_2H_5CO\cdot OMgBr + NaOH = C_2H_5CO\cdot ONa + MgBr(OH).$$

Lead Tetraethyl, $Pb(C_2H_5)_4$, is made commercially and is known in trade as "ethyl." It is a liquid and when added in small quantities to petrol constitutes an "anti-knock" material. It is excessively poisonous and when burnt with the petrol forms lead oxide, also a highly poisonous substance, which passes into the atmosphere in a fine state of division.

Questions on Chapter XVI

1. How are the primary, secondary, and tertiary phosphines prepared?

2. Compare the properties of the alkyl compounds of nitrogen, phosphorus, and arsenic.

3. Discuss the general structure of organic compounds possessing alkaline properties.

4. Describe the preparation of cacodyl, cacodyl oxide and chloride. Explain why cacodyl is to be regarded as a basic radical.

5. Compare the alkyl compounds of silicon with the paraffins. How is silico-pentane prepared?

6. Compare the behaviour towards oxidising agents of the alkyl compounds of the non-metals with those of the metals.

7. How is zinc ethyl obtained? Describe the action of water, ethyl alcohol, and the halogens on zinc ethyl.

8. Give examples of the uses of zinc ethyl in synthetic processes (preparation of paraffins and alcohols).

9. Explain the formation of secondary and tertiary alcohols from methyl magnesium iodide.

10. How is zinc ethyl prepared? Give equations to illustrate its value in organic synthesis, and describe briefly the properties of the substances obtained in the reactions you mention.

11. Describe the production and properties of the best known organo-arsenic compounds.

CHAPTER XVII

THE UNSATURATED HYDROCARBONS

The Unsaturated Hydrocarbons.—There are two important families of unsaturated hydrocarbons—**the olefines** and **acetylenes.** They contain less hydrogen than the paraffins with the same number of carbon atoms, and possess the characteristic property of uniting with other elements, forming **additive** compounds (p. 64). It is this property which has given rise to the term **unsaturated.**

The Olefines, C_nH_{2n}.—A list of the members of this family is given in Table X.

TABLE X.

THE OLEFINES, C_nH_{2n}.

		Boiling-point.
Ethylene (ethene)	$CH_2:CH_2$	−103°
Propylene (propene)	$CH_3\cdot CH:CH_2$	—
Butylene (butene)	C_4H_8	—
Ethylethylene, or α-butylene .	$C_2H_5\cdot CH:CH_2$	−5°
Dimethylethylene (symm.) or β-butylene	$CH_3\cdot CH:CH\cdot CH_3$	1°
Isobutylene	$(CH_3)_2C:CH_2$	−6°
Amylene (pentene)	C_5H_{10}	—
Methylethylethylene . . .	$CH_3\cdot CH:CH\cdot C_2H_5$	36°
Isopropylethylene	$(CH_3)_2CH\cdot CH:CH_2$	20°–21°
Methylethylethylene (unsymm.)	$(CH_3)(C_2H_5)C:CH_2$	31°–32°
Trimethylethylene	$(CH_3)_2C:CH(CH_3)$	36°–38°

General Properties of the Olefines.—The members of the series with 2, 3, and 4 carbon atoms are gases, like the corresponding paraffins. The higher members are colourless liquids and solids. The olefines are specifically lighter than water, in which they are but slightly soluble. In physical properties, therefore, they resemble the paraffins. Chemically they offer a marked contrast.

They burn with a luminous and rather smoky flame. They unite with hydrogen, halogen acids, halogens, strong or fuming sulphuric acid (indirectly also with water), hypochlorous acid, and finally they undergo oxidation with potassium permanganate and other oxidising agents.

We may take the best known member of the series—ethylene, C_2H_4—to illustrate the above reactions; for the present we will assign to it the formula $CH_2{:}CH_2$, indicating that the two carbons are united by a double bond in the same way that the union of oxygen and carbon is represented in ketones and aldehydes (p. 126).

Reactions of Ethylene.—1. Ethylene burns with a luminous and rather smoky flame as already shown in Expt. 25, p. 99.

2. When the olefines, mixed with hydrogen, are passed over platinum black, colloidal palladium, or finely divided nickel, at a high temperature, they unite with the hydrogen and form paraffins. Ethylene is converted into ethane—

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2 = \underset{\text{Ethane.}}{\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix}}$$

3. The olefines combine with chlorine, bromine, and (though less readily) with iodine, forming the chloride, bromide, and iodide of the olefine. Ethylene forms with chlorine, ethylene chloride, and with bromine, ethylene bromide (p. 250)—

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + Cl_2 = \underset{\text{Ethylene chloride.}}{\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix}}$$

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + Br_2 = \underset{\text{Ethylene bromide.}}{\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix}}$$

It should be noted that these substances are distinct from ethylidene chloride and bromide, which are obtained from acetaldehyde by the action of phosphorus chloride and bromide (p. 88).

EXPT. 91.—Prepare ethylene as described in Expt. 25 (p. 99), but collect the gas in gas bottles over water by means of a delivery tube attached to the flask in which the alcohol and sulphuric acid are heated. The gas bottles must then be stoppered and placed in an upright position. Fill two other gas bottles of the same dimensions, one with chlorine and the other with bromine vapour. Remove the stoppers

of the ethylene bottles and replace them by glass plates, and invert over them the bottles of chlorine and bromine from which the stoppers are also removed. On withdrawing the glass plate, the gases mix, and the colour of the chlorine and bromine quickly disappears. Colourless drops of oily liquid are then found on the sides of the bottles; they consist of ethylene chloride in one case and ethylene bromide in the other.

4. The olefines combine with hydrochloric, hydrobromic, and hydriodic acids—least readily with hydrochloric, most readily with hydriodic acid—forming alkyl halides. Ethylene passed into a strong solution of hydriodic acid is absorbed and forms ethyl iodide—

$$\begin{array}{l}CH_2\\ \| \\ CH_2\end{array} + HI = \begin{array}{l}CH_2I\\ | \\ CH_3.\end{array}$$

Ethyl iodide.

In the case of unsymmetrical compounds like propylene, $CH_3{\cdot}CH{:}CH_2$, with which the hydracid may unite in two different ways, the halogen atom attaches itself to the carbon with the fewest hydrogen atoms. Propylene forms with hydriodic acid mainly secondary propyl iodide, $CH_3{\cdot}CHI{\cdot}CH_3$, and not the primary compound, $CH_3{\cdot}CH_2{\cdot}CH_2I$.

5. The olefines combine with strong (more quickly with fuming) sulphuric acid, and form alkyl hydrogen sulphates. Ethylene forms ethyl hydrogen sulphate (p. 98)—

$$\begin{array}{l}CH_2\\ \| \\ CH_2\end{array} + H_2SO_4 = \begin{array}{l}CH_3\\ | \\ CH_2{\cdot}O{\cdot}SO_2{\cdot}OH.\end{array}$$

Ethyl hydrogen sulphate.

EXPT. 92.—Pour a few c.c. of fuming sulphuric acid into a glass tube about 25 cm. long closed at one end, introduce ethylene gas until most of the air is displaced, and close with a cork fitted with a glass tap (Fig. 66). On shaking and opening the tap under strong sulphuric acid, the liquid rises nearly to the top of the tube.

In this reaction the sulphuric acid dissociates into hydrogen and the group $—O{\cdot}SO_2{\cdot}OH$, which distribute themselves between the two unsaturated carbon atoms. In unsymmetrical olefines the group $—O{\cdot}SO_2{\cdot}OH$ usually attaches itself to the carbon with fewest hydrogen atoms. In other words, the more negative group attaches itself to the more positive carbon (viz. that linked with the larger number of alkyl groups). On hydrolysis these substances yield the corresponding alcohol—

$$CH_3{\cdot}CH_2O{\cdot}SO_3H + H_2O = CH_3{\cdot}CH_2OH + H_2SO_4.$$

This reaction is used in estimating the amount of olefines, or in removing them from a mixture with other gases or liquids, which, like the paraffins, are unabsorbed by the acid.

6. It has also been utilised for obtaining alcohol from coal-gas by absorbing the ethylene as ethyl hydrogen sulphate and decomposing the latter with water (see p. 190).

FIG. 66.

7. When the olefines are treated with a dilute solution of potassium permanganate, they undergo oxidation; in the first step of the process hydroxyl groups are added to the two unsaturated carbon atoms. Further oxidation converts the compounds thus obtained into other products, which will be considered elsewhere. Ethylene forms ethylene dihydroxide or glycol—

$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + H_2O + O = \begin{array}{l} CH_2{\cdot}OH \\ | \\ CH_2{\cdot}OH. \end{array}$$

Ethylene glycol

8. The olefines combine with hypochlorous acid (prepared from chlorine and water in presence of a copper compound) and form *chlorhydrins* of the olefines—

$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + HClO = \begin{array}{l} CH_2(OH) \\ | \\ CH_2Cl. \end{array}$$

Ethylene chlorhydrin.

9. They also unite with ozone to form *ozonides*.

$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + O_3 = \begin{array}{l} CH_2{\cdot}O \\ | \\ CH_2{\cdot}O \end{array}\!\!>\!O$$

Ethylene ozonide.

In addition to the above reactions ethylene unites with sulphur chloride with the formation of dichlorodiethyl sulphide (*mustard gas*) (see p. 199).

Sources of the Olefines.—The olefines are found among the products of the distillation of wood and coal, and are consequently present in coal-gas; but they are most readily obtained in a pure condition by the action of dehydrating agents (sulphuric

acid, phosphoric acid, or zinc chloride) on alcohols, or by heat alone (300°–500°) in presence of alumina. Ethyl alcohol yields ethylene—

$$C_2H_6O - H_2O = C_2H_4.$$

EXPT. 93. *Preparation of Ethylene and Ethylene Bromide from Ethyl Alcohol.*—The apparatus shown in Fig. 67 is convenient for this preparation (Calam). It consists of a round flask of about ½-litre capacity with a wide neck furnished with a treble-bored cork. A tube closed at the lower end for holding a thermometer is inserted through one hole, a tube ending in a spiral-shaped capillary as shown at *a* is inserted through a second hole, and a delivery tube through the third. The upper end of the spiral outside the flask is attached by rubber tubing to a long wide tube holding alcohol drawn out below and provided with a screw clip to adjust the flow of alcohol.

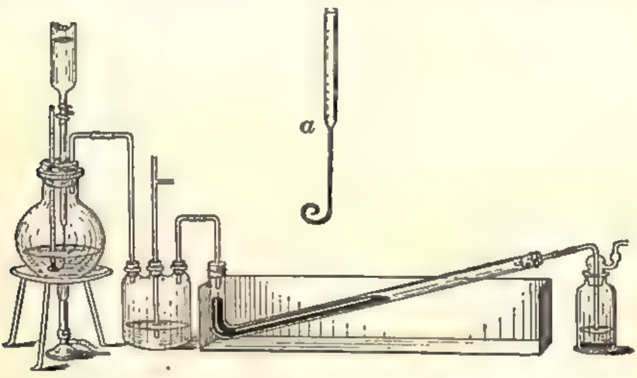


FIG. 67.—Preparation of Ethylene and Ethylene bromide.

A Woulff bottle is attached to the delivery tube which terminates below the first tubulus; through the second tubulus an open safety tube is inserted with a side piece near the upper end, and through the third tubulus a delivery tube which is attached to a wide bent tube lying in a metal trough, through which cold water flows. The upper end of this tube is connected to a wash-bottle. About 150 c.c. of glacial phosphoric acid are poured into the round flask, about 50 c.c. of bromine and 10 c.c. of water are introduced into the wide tube and 10 c.c. of bromine and 10 c.c of water into the end wash-bottle. The glacial phosphoric acid is heated to 190°–200°, and then 90-95 per cent. spirit is allowed to flow in slowly, the temperature being maintained at 200°. The phosphoric acid froths freely but does not froth over, and ethylene comes off rapidly. Gradually the bromine loses its colour, and finally a colourless liquid is obtained, which is ethylene bromide—

$$C_2H_4 + Br_2 = C_2H_4Br_2.$$

The ethylene bromide is then shaken up with a little carbonate of soda solution, dehydrated over calcium chloride, and distilled. The method of purification is that described in the preparation of ethyl bromide (p. 81). Ethylene bromide boils at 131° (p. 87).

The olefines are also obtained by running the alkyl halide into a strong solution of alcoholic potash. Ethyl iodide or bromide and alcoholic potash yields ethylene (p. 83)—

$$C_2H_5I + KOH = C_2H_4 + KI + H_2O.$$

EXPT. 94. *Preparation of Ethylene from Ethyl Iodide.*—Make a strong solution of caustic potash in methyl or ethyl alcohol (50 per

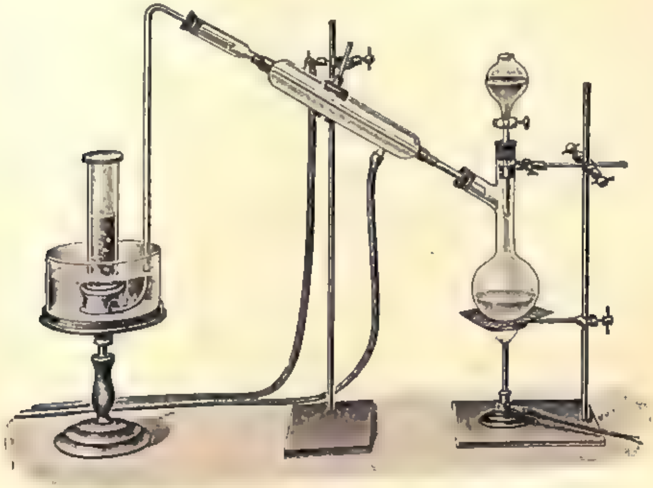


FIG. 68.—Preparation of Ethylene from Ethyl iodide.

cent. solution), and pour 50 c.c. of the solution into a distilling flask (250 c.c.), or place in the flask 20–30 grams of coarsely powdered caustic potash and cover it with a thin layer of alcohol. Attach the flask by the side-tube to an inverted condenser, and fix to the upper end of the condenser a bent delivery tube passing into a gas trough of water. A tap funnel containing 10–20 c.c. of ethyl iodide is inserted into the neck of the distilling flask. The apparatus is shown in Fig. 68. Warm the potash solution in the flask and then drop in the ethyl iodide. Gas is rapidly evolved and potassium iodide is deposited. When the air in the flask has been displaced, the ethylene may be collected and burnt.

A modification of this method is to pass the vapour of ethyl bromide or iodide over dry soda-lime contained in a silica tube gently heated by a Bunsen or Ramsay burner.

In the reaction just described a certain amount of ether is formed, the quantity of which depends upon the nature of the alkyl halide. When methyl iodide is decomposed with methyl alcoholic potash, the whole of the methyl iodide is converted into methyl ether.

$$CH_3I + KOCH_3 = CH_3{\cdot}O{\cdot}CH_3 + KI.$$

When an alcoholic solution of caustic alkali acts upon ethylene dibromide a substituted ethylene, **vinyl bromide** is the first product—

$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} + KOH = \begin{array}{l} CH_2 \\ \| \\ CHBr \end{array} + KBr + H_2O.$$

Further action results in the formation of acetylene (p. 259).

An interesting method for preparing olefines is the electrolysis of salts of dibasic acids, *i.e.* acids which contain two carboxyl groups (p. 334). Potassium succinate yields ethylene. The reaction resembles the formation of ethane from potassium acetate (p. 153)—

$$\underbrace{\begin{array}{l} CH_3 \vdots COO \vdots K \\ CH_3 \vdots COO \vdots K \end{array}}_{+\text{ electrode.}} \qquad \underbrace{\begin{array}{l} CH_2{\cdot} \vdots COO \vdots K \\ | \\ CH_2{\cdot} \vdots COO \vdots K \end{array}}_{+\text{ electrode.}}$$

Potassium acetate yields ethane. Potassium succinate yields ethylene.

Structure of the Olefines.—The readiness with which the olefines unite with other elements to form additive compounds indicates that the full valency of the carbon atoms is not brought into play, which is also the case with aldehydes, ketones and cyanides (p. 226). The question then arises: What is the function of the unemployed bonds in an unsaturated compound, and how should they be graphically represented? Are they inactive or free linkages (Formula I.) such as we usually associate with the formulæ of nitric oxide, —NO, and carbon monoxide, $=$CO, or, on the other hand, is the residual valency of the carbon atoms engaged in binding the two carbon atoms together by forming a double bond (Formula II.) such as we have tacitly assumed to exist between carbon and oxygen

in aldehydes and ketones or between carbon and nitrogen in cyanic and isocyanic esters (p. 228), mustard oils (p. 230), etc.?

Formula I.	Formula II.
$\begin{array}{l} -CH_2 \\ \;\;\vert \\ -CH_2 \end{array}$	$\begin{array}{l} CH_2 \\ \Vert \\ CH_2 \end{array}$
Ethylene with free bonds.	Ethylene with double bonds.

The question at first sight seems to have little real significance. Both formulæ explain the transition from unsaturated to saturated compounds, by the addition of new atoms or groups. In the first, the free bonds are at once brought into action; in the second, one of the double bonds must first be severed. On the other hand, the assumption of free bonds (Formula I.) presupposes the existence of substances like methyl, $-CH_3$, or methylene, $=CH_2$, which are unknown, and of two substances having the formula C_2H_4, viz. ethylene and ethylidene—

$\begin{array}{l} -CH_2 \\ \;\;\vert \\ -CH_2 \end{array}$	$\begin{array}{l} \;\;CH_3 \\ \;\;\vert \\ =CH. \end{array}$
Ethylene.	Ethylidene.

Each of the latter would give rise to a different bromine derivative, viz. ethylene and ethylidene bromide, whereas only one compound, C_2H_4, exists, yielding ethylene bromide.

Theory of the Double Bond.—The principal grounds upon which the theory of the double bond rests are: first, the olefines and, in fact, all unsaturated compounds, unite with an even number of univalent atoms or groups—in other words, the saturation of one unsaturated carbon atom necessitates that of the other; secondly, the unsaturated carbon atoms invariably adjoin one another. There is an evident connection of a special kind between the two unsaturated carbon atoms, for which the device of the double bond is made to serve.

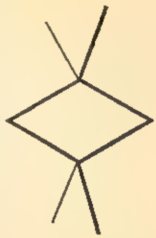


FIG. 69.

We must be careful, however, to recognise clearly that the method of indicating this relationship is not taken to imply a firmer connection between the unsaturated carbon atoms, but that, on

the contrary, a double bond is a point of weakness in the molecule rather than of strength. For example, the heat of combustion of ethane is 370 calories, that of the molecule of hydrogen 138 calories. From this the heat of combustion of ethylene should be 232 calories, whereas actually it is 333 calories, showing that less energy is expended in breaking up the molecule, that is, in separating the two atoms of carbon than in ethane. Various theories, giving prominence to this idea, have been advanced, resting mainly on the space arrangement of the carbon bonds (Fig. 52, p. 116). Thus, if we suppose the bonds to diverge at equal angles (109·5°) from the central carbon atom, and to retain their positions when the two carbon atoms are doubly linked, the space arrangement viewed in perspective will appear as in Fig. 69.

If a bond represents the direction in which a force acts, the resultant of two forces acting at an angle of 109·5° will not be the equivalent of the same forces acting in a straight line. According to another theory, if the result of double linking tends to bend the two pairs of bonds from their original positions into a straight line joining the two carbon atoms, a condition of strain will be set up, which will be a cause of instability (Baeyer's strain theory).

This theory has been developed so as to account for the fact that rings of 5 and 6 carbon atoms appear to be more stable than those with more or fewer, since the displacement of the bonds from the natural angle 109·5° is less in such rings, as may be seen from the following table (see p. 365)

Carbon atoms.	Ring compound.	Angle of the ring.	Displacement of natural angle.	
2	Ethylene	0°	109·5°	con-traction
3	Cyclopropane	60°	49·5°	
4	Cyclobutane	90°	19·5°	
5	Cyclopentane	108°	1·5°	
6	Cyclohexane	120°	10·5°	expan-sion
7	Cycloheptane	128·5°	19·1°	
8	Cyclo-octane	135°	25·5°	

Nomenclature of the Olefines.—The names of the olefines are derived from those of the alkyl groups containing the same number of carbon atoms, to which the end syllable *-ene* is added (see

Table X) (p. 246). The general term olefine is sometimes replaced by the word **alkylene.**

The isomeric olefines, such as the butylenes and amylenes, are designated as derivatives of ethylene and are readily distinguished in this way. The symbol Δ is used for a double bond, and numerals indicate the position at which a double bond begins. For example, the hydrocarbon isoprene (p. 256) is 1-methylΔ1 : 3-butadiëne.

$$\begin{array}{c} {\scriptstyle (1)\quad (2)(3)\quad (4)} \\ CH_2{:}C{\cdot}CH{:}CH_2 \\ | \\ CH_3 \\ {\scriptstyle (1)} \end{array}$$

The Greek letters, α, β, γ, etc., are also employed to indicate the position of the double bond, the letter denoting the one unsaturated carbon atom which lies nearest to the end of the chain (the end carbon atom is α, the next β, etc.). Thus, ethyl ethylene, $CH_3{\cdot}CH_2{\cdot}CH{=}CH_2$, is α-butylene, whilst dimethyl ethylene, $CH_3{\cdot}CH{=}CH{\cdot}CH_3$, is β-butylene.

The official names of the olefines are *alkenes*. Thus ethylene is *ethene*. When more than one double bond is present in the molecule the number is indicated by a Greek numeral. Thus buta*di*ene is $CH_2{:}CH{\cdot}CH{:}CH_2$.

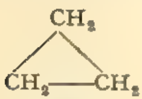
Special Members of the Olefines.—It has already been stated that methylene, CH_2, is unknown, but may have a momentary existence.

Olefines are obtained commercially from natural gas, derived from petroleum and from gas obtained in cracking petroleum. They are used extensively for the synthesis of other products. Ethylene can be used for the production of alcohol and propylene for producing glycerol and acetone. The conversion of olefines to aromatic hydrocarbons is important in the production of aviation spirit, while the polymerisation of butylenes and other olefines yields useful lubricants and plastic materials such as synthetic rubber and electrical insulators.

Ethylene, Olefiant Gas, $CH_2{:}CH_2$.—The name olefiant, or oil-forming, gas is connected with its power of uniting with chlorine to form ethylene chloride, oil of the Dutch chemists. The liquid was known at one time as *Dutch liquid*, and the term *olefiant* has given rise to the word *olefine*, the present name of the family. The chief methods of preparation and properties of ethylene have

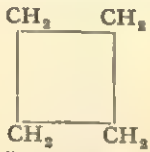
already been fully described. Ethylene may be liquefied at 0° under a pressure of 44 atmospheres, and boils at − 103°. When allowed to evaporate in a vacuum, the temperature falls to − 150°. It was by the aid of liquid ethylene that Dewar succeeded in liquefying considerable quantities of oxygen and nitrogen. Ethylene and also a small quantity of other olefines are present, to the extent of 4–5 per cent., in coal gas. The volume is readily ascertained by passing a measured quantity of coal-gas into fuming sulphuric acid, by which ethylene is rapidly absorbed. The Hempel apparatus is convenient to use for this purpose, the fuming acid being contained in a pipette of a similar construction to that shown in Fig. 43, p. 70.

Saturated Hydrocarbons which are Isomeric with the Olefines.—An important class of hydrocarbons, isomeric with the olefines, has been prepared and carefully studied in recent years. They are much more stable than the olefines, and, with the exception of the lowest member, C_3H_6, closely resemble the paraffins in physical and chemical properties. These substances are known as tri-, tetra-, penta-methylene, etc., or cyclo-propane, -butane, -pentane, etc., and are represented as **ring compounds**, with the following structural formulæ—



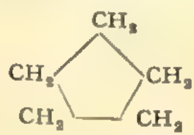
Trimethylene, or Cyclopropane.

etc.,



Tetramethylene, or Cyclobutane.

etc.



Pentamethylene, or Cyclopentane.

Hexamethylene, or cyclohexane, and its alkyl derivatives are found in petroleum, and are known as *naphthenes*.

The highest member of the series is cyclononane, C_9H_{18}. For further details a larger treatise must be consulted.

Diolefines and Polyenes.—*Isoprene*, or *methyl butadiene*, $CH_2{:}C(CH_3){\cdot}CH{:}CH_2$, originally obtained by distilling rubber and *butadiene*, $CH_2{:}CH{\cdot}CH{:}CH_2$, obtained respectively from isoamyl and butyl alcohol, polymerise in presence of metallic sodium, yielding *synthetic rubber* closely resembling, if not identical with, the natural product (p. 511). Rubber is therefore a polyolefine or *polyene* consisting of a long chain of isoprene groups. Similar polyene chains are present in many natural products, such as the pigments bixin (annatto seeds), lycopene (tomatoes), carotene (carrots), crocetin (saffron), etc.

The Acetylenes, C_nH_{2n-2}.—A list of the lower members of the series is given in Table XI.

TABLE XI.

THE ACETYLENES, C_nH_{2n-2}.

		B.p.
Acetylene, or ethine	$CH{\vdots}CH$	Gas
Methyl acetylene, propine, or allylene	$CH_3{\cdot}C{\vdots}CH$	,,
Ethyl acetylene	$C_2H_5{\cdot}C{\vdots}CH$	18°
Propyl acetylene	$C_3H_7{\cdot}C{\vdots}CH$	40°
Dimethyl acetylene, butine or crotonylene	$CH_3{\cdot}C{\vdots}C{\cdot}CH_3$	29°

Nomenclature of the Acetylenes.—The name of the group is derived from that of the first and most important member, acetylene, C_2H_2. The names of the individual members are most conveniently designated as alkyl derivatives of acetylene, on the plan adopted in the nomenclature of the olefines. Another method is to add the end syllable *ine* to the root of the name of the paraffin with the same number of carbon atoms. Thus, acetylene is called ethine; methyl acetylene, propine, etc. Some of the members have, in addition, certain special names, which are derived from the names of unsaturated radicals to which the acetylenes are related. Allylene, C_3H_4, is derived from the radical allyl, C_3H_5, etc. (p. 267).

Structure of the Acetylenes.—The acetylenes contain 2 hydrogen atoms less than the olefines, or 4 hydrogen atoms less than the paraffins. The relation of ethane, ethylene, and acetylene is represented as follows:—

C_nH_{2n+2} Paraffin.	C_nH_{2n} Olefine.	C_nH_{2n-2}. Acetylene.
C_2H_6 Ethane.	C_2H_4 Ethylene.	C_2H_2. Acetylene.

For similar reasons to those which have been advanced in the case of the olefines (p. 253), the unsaturated carbon atoms in the acetylenes are assumed to be linked by a treble bond, like carbon and nitrogen in hydrocyanic acid and the cyanogen compounds (p. 224). Thus, each carbon atom of the group has one bond free, which is united to hydrogen or an alkyl group. The union of the unsaturated carbon atoms in the acetylenes is still less stable than that of the double bond in the olefines, and the

space arrangement shown in Fig. 70 has the same significance as that represented in the case of the olefines (Fig. 69).

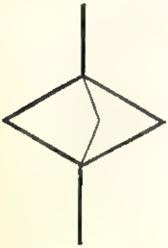


FIG. 70.

In many respects the acetylenes resemble the olefines, but the former undergo change more readily, and generally speaking show less stability. Just as in the case of ethylene, the heat of combustion of acetylene is higher (310 cals.) than that obtained by deducting the value for a molecule of hydrogen from the heat of combustion for ethylene (195 cals.). Acetylene, the most important member, serves as a type of the whole group, and will alone be considered in detail.

Acetylene, CH⋮CH.—Acetylene was first observed by E. Davy (1836), but was more carefully studied by Berthelot (1859), who prepared it by the direct union of carbon and hydrogen by sparking carbon electrodes in an atmosphere of hydrogen. The apparatus used by Berthelot is shown in Fig. 71. It consists of a pear-shaped

FIG. 71.—Formation of Acetylene from Carbon and Hydrogen.

bulb closed at each end by a double-bored stopper. Carbon electrodes are inserted through two opposite holes of the stopper, whilst, through the other two holes, glass tubes are inserted for conducting a current of hydrogen through the bulb. Acetylene is also formed by the incomplete combustion of hydrocarbons; coal-gas, for example, produces acetylene when a Bunsen burner "strikes back" and burns within the metal tube.

EXPT. 95.—Arrange the apparatus shown in Fig. 72. It consists of a glass funnel, bent twice at right angles, and dipping into a cylinder containing an ammoniacal solution of cuprous chloride. A Bunsen burner is lighted at the pinhole jet within the tube, and placed below the funnel. A current of air is then aspirated through the apparatus.

In a short time a red precipitate of copper acetylide, $C_2Cu_2H_2O$, is deposited in the cylinder containing the copper solution. The ammoniacal solution of cuprous chloride is prepared by boiling strong hydrochloric acid with copper oxide and metallic copper until the liquid is transparent and nearly colourless. The solution is then poured into water, and the precipitate of cuprous chloride is washed once or twice by decantation, and then dissolved in a strong solution of ammonium chloride. When required, a little of the liquid is taken, and sufficient ammonia is added to give a clear, deep blue solution.

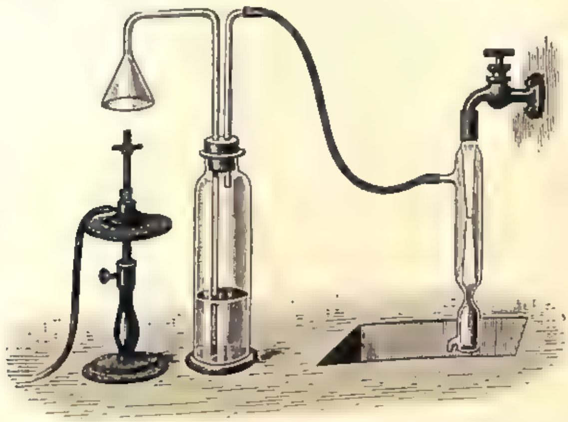


FIG. 72.—Acetylene formed by incomplete combustion of coal-gas.

Acetylene is also obtained by the action of alcoholic potash on ethylene bromide. The process occurs in two steps; monobromethylene, or vinyl bromide, is first formed, and the latter then loses hydrobromic acid and forms acetylene—

$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} + KOH = \underset{\text{Vinyl bromide, or Monobromethylene.}}{\begin{array}{l} CHBr \\ \| \\ CH_2 \end{array}} + KBr + H_2O.$$

$$\begin{array}{l} CHBr \\ \| \\ CH_2 \end{array} + KOH = \underset{\text{Acetylene.}}{\begin{array}{l} CH \\ \equiv \\ CH \end{array}} + KBr + H_2O.$$

EXPT. 96.—Fit up an apparatus similar to that drawn in Fig. 68; but instead of collecting the gas in a gas-trough, allow it to bubble through an ammoniacal solution of cuprous chloride, contained in a

beaker. Pour 50 c.c. of a strong solution (50 per cent., made by dissolving 25 grams of KOH in a few c.c. of water and making up to 50 c.c. with methyl alcohol) of alcoholic caustic potash into the flask, and heat it gently. When ethylene bromide is dropped in from the tap-funnel a rapid evolution of acetylene occurs, and copper acetylide is deposited in the copper solution.

Acetylene is now used as an illuminant, and for this purpose is obtained by the action of water upon calcium carbide—

$$Ca\boxed{C_2 + H_2}O + H_2O = C_2H_2 + Ca(OH)_2.$$

Calcium carbide, or calcium acetylide, was first produced commercially by Willson, an American (1892), and was also obtained by Moissan by the aid of his electric furnace. It is prepared by fusing a mixture of lime and coke by means of a powerful electric current—

$$3C + CaO = \underset{\text{Calcium carbide.}}{CaC_2} + CO.$$

The various electric furnaces in which carbide is manufactured are constructed on the same principle. The heat of the arc produced by the passage of the current between the bed of the furnace which forms the positive electrode and a carbon rod, or bundle of rods, which forms the negative electrode, fuses the mixture of coke and lime in which the electrodes are embedded. Various forms of furnaces are used, in some of which the charges are introduced and the product removed intermittently; in others the process is continuous, and the fused carbide runs away as it is formed. A carbide furnace in its simplest form is shown in Fig. 73. It consists of a graphite crucible in contact with a metal plate, *a*, which forms the positive electrode, and a carbon rod, *b*, which forms the negative electrode, the intermediate space being filled up with the coke and lime mixture.

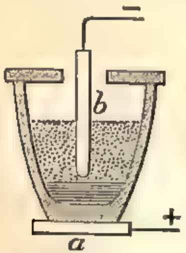


FIG. 73.—Formation of Calcium carbide.

EXPT. 97.—Add a few drops of water to some calcium carbide contained in a test-tube. Rapid effervescence ensues, and the gas, which is evolved, may be lighted at the mouth of the tube. Acetylene burns with a white, intensely luminous and rather smoky flame. The gas obtained from the carbide emits a smell of phosphine, which is due to traces of phosphate in the limestone becoming reduced to calcium phosphide. The latter is decomposed by water, and forms phosphine. For obtaining larger quantities of the gas for experimental illustration,

a flask is furnished with a tap-funnel and delivery tube. A layer of sand is placed on the bottom of the flask and small pieces of carbide above this. Water is then added drop by drop from the tap-funnel. The gas can be collected over water.

Properties of Acetylene.—Acetylene is a colourless gas which, in the pure state, has an unpleasant smell of garlic, quite unlike the smell of a Bunsen burner when it is "burning down," or of the gas given off from commercial carbide. Water dissolves its own volume, and acetone 31 times its own volume, of acetylene at 0° and 760 mm. and 300 times its own volume at 12 atmospheres. This solution, unlike the liquid acetylene, may be safely stored in metal cylinders, and when burnt with oxygen in a blow-pipe flame gives a temperature which readily melts steel and is used for cutting that metal.

FIG. 74.

EXPT. 98—The absorption of acetylene by acetone may be shown in the following way: a glass tube about 60 cm. long and 1·7 cm. inside diameter, and closed at one end is filled with acetylene. The tube is at once closed by a tap-funnel inserted through a cork fitted to the open end (Fig. 74). About 30 c.c. of acetone are cautiously introduced into the tube through the tap-funnel taking care that no air enters. The contents are well shaken when the bulk of the acetylene is absorbed. If the tap-funnel is now filled with water and the apparatus inverted in a basin of water. On opening the tap the water will rise rapidly in the tube and fill it three parts full.

Acetylene burns with a smoky and very hot flame. For illuminating purposes, complete combustion is effected by using fine pin-hole burners, which produce a thin, flat flame, having a proportionately large surface. It has about 15 times the illuminating power of coal-gas. Acetylene has been liquefied under a pressure of 26 atmospheres at 0°, and the liquid has a specific gravity of 0·45. A mixture with air containing from 3 to 65 per cent. of acetylene explodes violently when fired. Even the pure gas when compressed or in the liquid state, explodes on heating, or by detonation. For illuminating purposes it is therefore necessary to have the gas supply well-cooled. The principle upon which the various forms

of acetylene generators are constructed is to admit water to the carbide, or to add carbide gradually to the water, and to collect the gas in a gas-holder over water. By the first method the gas-holder, on filling, automatically shuts off the supply of water to the carbide, and so stops the evolution of gas. As the gas-holder empties, fresh water enters the vessel containing the carbide, and the process is repeated until the charge of carbide is exhausted. By the second method, the carbide is added by hand or automatically to a reservoir containing water, from which the gas passes to a gas-holder. Traces of phosphine are generally present in commercial acetylene, and produce, on burning, fumes of phosphorus pentoxide. The phospine is removed by oxidising agents, such as bleaching powder, chromic acid mixtures, etc.

When acetylene is heated to a red heat, it is completely decomposed into hydrogen and carbon, the latter being deposited as soot. At lower temperatures acetylene appears to polymerise and form benzene, according to the equation—

$$3C_2H_2 = \underset{\text{Benzene.}}{C_6H_6}.$$

This operation is most effectively conducted by passing the gas over a long layer of finely divided nickel at a temperature of 150° and collecting the product in a U-tube surrounded by a freezing mixture. The oily liquid which is condensed contains a small amount of benzene. (Sabatier.)

The unstable nature of acetylene depends on the fact that it is an endothermic substance, *i.e.*, it is formed with absorption of heat, which, on disintegration of the molecule, is given off as heat energy.

A characteristic property of acetylene is the formation of compounds with copper and silver known as *acetylides* of copper and silver. They are deposited as amorphous precipitates by passing the gas into ammoniacal solutions of cuprous chloride and silver nitrate respectively; the copper compound is red, that of silver, white. The substances have the formulæ—

$$\underset{\text{Copper acetylide.}}{C_2Cu_2H_2O.} \qquad \underset{\text{Silver acetylide.}}{C_2Ag_2H_2O.}$$

They are extremely explosive in the dry state, especially the silver compound. When decomposed with potassium cyanide or hydrochloric acid, acetylene is liberated.

Mono- and di-sodium acetylides, C_2HNa and C_2Na_2, are also known and are obtained by passing the gas over heated sodium.

The formation of copper and silver compounds is associated with the presence of a $\equiv CH$ group. Methyl acetylene forms a compound, $CH_3{\cdot}C\equiv CAg$; dimethylacetylene, $CH_3{\cdot}C\equiv C{\cdot}CH_3$, on the other hand, forms no metallic derivative. The acid character of acetylene or its property of forming metallic compounds may be connected with the presence of an unsaturated carbon atom, such as we find to be the case in hydrocyanic acid, $HC\equiv N$ (p. 213).

Additive Compounds of Acetylene.—Acetylene, like ethylene, forms additive compounds with hydrogen, halogen acids, the halogens, and water.

1. When acetylene mixed with hydrogen is passed over platinum black or finely divided nickel at the ordinary temperature, it is converted into ethylene and then into ethane—

$$CH\vdots CH + H_2 = CH_2{:}CH_2.$$
$$CH_2{:}CH_2 + H_2 = CH_3{\cdot}CH_3.$$

2. Acetylene unites with two molecules of halogen acid. The addition occurs in two steps. The two halogen atoms attach themselves to the same carbon atom, and thus form ethylidene compounds—

$$CH\vdots CH + HI = \underset{\text{Vinyl iodide.}}{CH_2{:}CHI.}$$
$$CH_2{:}CHI + HI = \underset{\text{Ethylidene iodide.}}{CH_3{\cdot}CHI_2.}$$

3. Acetylene is rapidly absorbed by the halogens. Acetylene and bromine form acetylene dibromide and then tetrabromide—

$$CH\vdots CH + Br_2 = \underset{\text{Acetylene dibromide.}}{CHBr{:}CHBr.}$$
$$CHBr{:}CHBr + Br_2 = \underset{\text{Acetylene tetrabromide.}}{CHBr_2{\cdot}CHBr_2.}$$

EXPT. 99. *Preparation of Acetylene Tetrabromide.*—Fill a gas-holder with acetylene, and bubble the gas through a U-tube containing bromine cooled in ice. After a time the bromine is decolorised. The heavy, colourless liquid which is formed is acetylene tetrabromide. It is purified like ethylene bromide in Expt. 93, p. 250. *Acetylene tetrachloride*, $C_2H_2Cl_4$, and the *trichloride*, $C_2H_3Cl_3$, are now produced as commercial products for use as solvents, etc. (p. 93).

4. Acetylene and its homologues containing a $\vdots$CH group may be induced to combine with the elements of water by the action of strong sulphuric acid, followed by the addition of water, or by passing the gas into a mixture of mercuric oxide or a mercuric salt and dilute sulphuric acid according to the following equation—

$$CH\vdots CH + H_2O = CH_3{\cdot}CHO.$$

The aldehyde prepared in this way has been utilised commercially for the manufacture of acetic acid by oxidation and ethyl alcohol by reduction.

5. Acetylene also combines with acetic acid in presence of a catalyst (a mercury salt) to form vinyl acetate, which finds certain industrial applications—

$$\underset{\text{Vinyl acetate.}}{C_2H_2 + CH_3{\cdot}CO_2H = CH_2{:}CH{\cdot}CH_2{\cdot}COOH.}$$

EXPT. 100.—Pass acetylene through a solution of 1 gram of mercuric sulphate in 50 c.c. of 10 per cent. sulphuric acid contained in a flask which is immersed in an outer vessel of warm water at a temperature of about 40°. After the gas has passed through for 10–15 minutes filter the liquid, neutralise it with sodium carbonate and test for acetaldehyde by the nitroprusside reaction (p. 140).

Dipropargyl, C_6H_6, though not belonging strictly to the acetylene series, has a special interest from the fact that it is isomeric with benzene. Dipropargyl is prepared from diallyl, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$ (p. 268), which contains two double bonds, and therefore unites with 2 molecules of bromine. The tetrabromide has the formula—

$$CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br.$$
Diallyl tetrabromide.

When decomposed by alcoholic potash, it loses 4 molecules of hydrobromic acid and forms dipropargyl, which consequently has the following formula—

$$CH\vdots C{\cdot}CH_2{\cdot}CH_2{\cdot}C\vdots CH.$$
Dipropargyl.

It is a liquid which boils at 85°, and has a specific gravity of 0·81, whereas benzene boils at 81°, and has a specific gravity of 0·880. Dipropargyl offers a marked contrast to benzene in forming additive compounds with 4 molecules of the halogen acids and halogens of the general formula $C_6H_{10}X_4$ and $C_6H_6X_8$ (X stands

for the halogen), which may be regarded as derivatives of hexane, C_6H_{14}. Benzene, on the other hand, forms additive compounds only with the halogens, not with the halogen acids, and in the former case combines with not more than 3 molecules. Benzene hexachloride has the formula $C_6H_6Cl_6$.

Questions on Chapter XVII

1. Give a method for preparing ethylene. Name three of its characteristic properties.

2. Devise a method for preparing alcohol from the elements carbon and hydrogen.

3. Compare the properties of the paraffins, olefines, and acetylenes.

4. Describe a method for preparing propylene. What products are obtained when propylene is acted on by bromine, hydriodic acid, and sulphuric acid? Give the structural formulæ of the products.

5. Explain why a double bond is weaker than a single bond.

6. Why is ethylene represented as containing carbon atoms united by a double bond?

7. What class of saturated hydrocarbons are isomeric with the olefines?

8. How would you separate ethylene from ethane in a mixture of the two gases, and how would you identify ethylene?

9. Describe a method by which ethyl iodide may be converted into ethylene, and *vice versa*.

10. In what way can acetylene be distinguished from ethylene?

11. What is dipropargyl? What relation does it bear to benzene?

12. Explain what is meant by the term unsaturated compound. How are such compounds identified?

13. Given 10 c.c. of a gas which is either marsh gas or ethylene, how would you experimentally determine the composition of the gas?

14. State concisely the chemical reasons for concluding that ethylene should be represented by the formula C_2H_4 and not by the formula CH_2.

15. Draw a diagram of the apparatus required in the preparation of ethylene dibromide, and state the method of procedure.

16. Starting with acetylene, show how ethylene, ethyl alcohol, and so-called cuprous acetylide may be obtained from it.

17. How is acetylene best obtained? Compare the action of bromine upon this compound with its action on marsh gas and ethylene respectively.

CHAPTER XVIII

DERIVATIVES OF THE UNSATURATED HYDROCARBONS

Compounds with Multiple Functions.—We have up to the present considered in some detail the properties of certain families of compounds. It may have been observed that in their behaviour towards reagents the paraffins resemble hydrogen. Both the paraffins and hydrogen are only acted upon (at the ordinary temperature and in daylight) by chlorine and bromine. In the same way the atom of hydrogen in certain compounds resembles the alkyl groups, inasmuch as the one may replace the other in the various homologous series without greatly influencing the chemical character of the compound. This is evident from a comparison of the lowest members of a series, *e.g.*, formaldehyde and acetaldehyde, formic acid and acetic acid, ammonia and trimethylamine—

$H{\cdot}CHO$	$H{\cdot}COOH$	$H_3N.$
$CH_3{\cdot}CHO$	$CH_3{\cdot}COOH$	$(CH_3)_3N.$

It is not therefore the hydrogen atom or the alkyl group (which replaces it in these compounds) that determines the difference in chemical properties which are the distinguishing features of the various families of compounds, but the presence of such elements or groups as the halogens, hydroxyl, aldehyde, ketone, carboxyl, amino, cyanogen, olefine, and acetylene groups.

In this and subsequent chapters we shall treat of compounds which contain more than one of the above groups. The study of these compounds is facilitated by the knowledge that each group retains its specific characters for the most part unchanged in the presence of other groups.

It follows, therefore, that a compound with more than one group possesses, so to say, more than one set of properties. It has, what we may term, a *multiple function*, which means that it combines the properties of all the groups present. Moreover, if we know the character of the groups in the compound, it is possible to predict with some certainty the chemical behaviour of the compound.

The first examples which we shall study are the derivatives of

the unsaturated hydrocarbons. These hydrocarbons form, like the paraffins, halogen derivatives, alcohols, aldehydes, acids, etc., and yet retain the property of forming additive compounds, like the olefines and acetylenes.

Derivatives of the Olefines.—The simplest of these are the vinyl compounds containing the radical $CH_2{:}CH'$. Vinyl alcohol $CH_2{:}CH{\cdot}OH$ is obtained together with the unsaturated ketone (ketene) $CH_2{:}C{:}O$ by passing acetone through a red-hot tube containing broken pot. We shall select for purposes of illustration some of the derivatives of propylene. These compounds may be either named after the olefines, from which they are derived, or designated as compounds of an unsaturated univalent radical. The name allyl (from *allium*, garlic, which contains allyl sulphide) is given to the radical $CH_2{:}CH{\cdot}CH_2'$, and the compound $CH_2{:}CH{\cdot}CH_2Cl$ is called allyl chloride; whereas the isomeric substances $CHCl{:}CH{\cdot}CH_3$ and $CH_2{:}CCl{\cdot}CH_3$ are distinguished by the names α- and β-chloropropylene respectively.

Allyl Compounds.—The allyl compounds are obtained directly or indirectly from glycerol. Allyl chloride and bromide are prepared from allyl alcohol, $CH_2{:}CH{\cdot}CH_2OH$ (see below), by the usual methods for converting alcohols into halogen compounds—*i.e.*, by the action of phosphorus chloride or bromide.

Allyl Iodide, $CH_2{:}CH{\cdot}CH_2I$, is most readily obtained from glycerol by the action of yellow phosphorus and iodine—

$$\underset{\text{Glycerol.}}{C_3H_5(OH)_3} + I + P = \underset{\text{Allyl iodide.}}{C_3H_5I} + P(OH)_3.$$

The glycerol and iodine are mixed in a retort attached to a condenser, and the phosphorus is gradually added, whilst a current of carbon dioxide is passed through the apparatus. A violent reaction occurs and the allyl iodide distils. It is purified in the same manner as ethyl bromide (p. 81). Further action results in the addition of hydrogen iodide to form propylene di-iodide $CH_3{\cdot}CHI{\cdot}CH_2I$, which then undergoes reduction to isopropyl iodide $CH_3{\cdot}CHI{\cdot}CH_3$. Allyl iodide is a colourless liquid with an odour of garlic. It boils at 101°.

Being unsaturated, it combines with the halogens and halogen acids. On the other hand, it undergoes reactions like an alkyl iodide. It gives with potassium cyanide, allyl cyanide; with potassium sulphide, allyl sulphide; and with potassium thiocyan-

ate, allyl thiocyanate, whilst with metallic sodium it forms diallyl, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$.

Allyl Sulphide, $(C_3H_5)_2S$, is a constituent of garlic (*Allium sativum*), to which it gives the characteristic odour, and is sometimes termed *oil of garlic*. It has been prepared in the manner described above, by distilling allyl iodide and potassium sulphide—

$$\underset{\text{Allyl iodide.}}{2C_3H_5I} + K_2S = \underset{\text{Allyl sulphide.}}{(C_3H_5)_2S} + 2KI.$$

Allyl Isothiocyanate, Oil of Mustard.—The oil was first obtained from black mustard seed, and gives its name to the family of mustard oils (p. 230). It is present in the seed as a glucoside, known as *sinigrin* or *potassium myronate*, associated with a hydrolytic ferment, *myrosin*. The myrosin plays the part of emulsin in bitter almonds (p. 212), *i.e.*, when the seed is crushed with water, hydrolysis occurs and the glucoside is broken up into glucose, potassium hydrogen sulphate, and allyl isothiocyanate. The same decomposition is produced by dilute mineral acids—

$$\underset{\text{Potassium myronate.}}{C_{10}H_{16}NS_2O_9K} + H_2O = C_6H_{12}O_6 + KHSO_4 + \underset{\text{Allyl isothiocyanate.}}{C_3H_5N{\cdot}CS}.$$

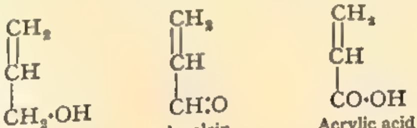
Oil of mustard has been synthesised from allyl iodide and potassium thiocyanate. Allyl thiocyanate is first formed, which on distillation undergoes intramolecular change and yields the isothiocyanate liquid, boiling at 151° and possessing a sharp and pungent taste and smell.

Allyl Alcohol, $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, is prepared by heating glycerol with oxalic acid. This reaction resembles that by which formic acid is obtained (p. 157), but it differs from it in certain important respects. The compound first formed is the same in both processes, viz. glycerol oxalic acid ester; but the temperature at which the product is distilled is much higher (200°–220°) in the case of allyl alcohol. At this temperature, the acid oxalic ester is transformed into the neutral ester which decomposes into allyl alcohol and carbon dioxide—

$$\begin{array}{l} CH_2{\cdot}O{\cdot}CO{\cdot}CO_2H \\ | \\ CH(OH) \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{l} CH_2{\cdot}O{\cdot}CO \\ |\qquad\quad | \\ CH{\cdot}O{\cdot}CO \\ | \\ CH_2OH \end{array} \longrightarrow \underset{\text{Allyl alcohol.}}{\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array}} + 2CO_2.$$

It will be observed that it is the glycerol which yields the allyl alcohol and not the oxalic acid, whereas in the preparation of formic acid, the oxalic acid undergoes decomposition and the glycerol is unchanged. The proportion of glycerol used in the present case is consequently much larger.

Allyl alcohol is a colourless liquid with a pungent smell and boils at 96°. It combines the properties of an olefine and an alcohol. On the one hand, it forms additive compounds with the halogens, and may be converted by gentle oxidation with potassium permanganate into glycerol, just as ethylene is converted into glycol (p. 249). On the other hand, it shows the characteristics of a primary alcohol, and with energetic oxidising agents may be converted into an aldehyde, acrylaldehyde, or acrolein, and then into a monobasic acid, acrylic acid—



Allyl alcohol. Acrolein. Acrylic acid

EXPT. 101. *Preparation of Allyl Alcohol.*—Distil a mixture of 50 grams of oxalic acid and 200 grams of glycerol from a retort, which is attached to a condenser and receiver. Continue heating until the temperature reaches 180°. Change the receiver and continue the distillation until 260° is reached. The first distillate contains some formic acid, the second distillate consists of impure allyl alcohol. The latter is redistilled until the temperature reaches 105°. The distillate is dehydrated with solid potassium carbonate, and the liquid removed and redistilled. Add bromine water to a little of the allyl alcohol. It is immediately decolorised from the formation of α-β-dibromopropyl alcohol, $CH_2Br{\cdot}CHBr{\cdot}CH_2OH$.

Acrolein, Acrylaldehyde, $CH_2{:}CH{\cdot}CHO$, is most easily obtained by distilling a mixture of glycerol and potassium hydrogen sulphate. The latter acts as a dehydrating agent—

$$C_3H_5(OH)_3 - 2H_2O = \underset{\text{Acrolein.}}{C_3H_4O}.$$

EXPT. 102.—Mix together 3 parts of glycerol, 10 parts of crystallised potassium bisulphate and 2 parts of potassium sulphate in a test-tube and heat the mixture. The vapour given off attacks the eyes and mucous membrane. If the experiment is conducted on a larger scale, a capacious retort must be taken, as the mixture froths on heating.

A mixture of 100 grams of glycerol, 330 parts of crystallised potassium bisulphate and 66 parts of potassium sulphate is introduced, heated to 195° and stirred. The retort is connected with a condenser and receiver. The distillate is fractionated and dehydrated over calcium chloride.

Acrolein is a colourless liquid which boils at 52°. It has the properties of an aldehyde, reducing alkaline solutions of silver and copper. It can be reduced to allyl alcohol and oxidised to acrylic acid. Its olefinic character is shown by the fact of its combining with the halogens and halogen acids. With bromine, dibromopropionaldehyde is formed—

$$CH_2{:}CH{\cdot}CHO + Br_2 = \underset{\text{Dibromopropionaldehyde.}}{CH_2Br{\cdot}CHBr{\cdot}CHO.}$$

Acrolein has a penetrating smell, and attacks the eyes. The unpleasant smell of burnt fat is due to the decomposition of the glycerol of the fat and the formation of acrolein.

Acrylic Acid, $CH_2{:}CH{\cdot}CO{\cdot}OH$, is the simplest member of the important group of unsaturated fatty acids. It is formed in a variety of ways; by the oxidation of acrolein; by the action of alcoholic potash on α- or β-bromopropionic acid, and by heating hydracrylic acid, or hydroxypropionic acid, $CH_2(OH){\cdot}CH_2{\cdot}COOH$, to which reference will be made later (p. 323)—

$$\underset{\alpha\text{-Bromopropionic acid.}}{CH_3{\cdot}CHBr{\cdot}COOH} + KOH = \underset{\text{Acrylic acid.}}{CH_2{:}CH{\cdot}COOH} + KBr + H_2O.$$

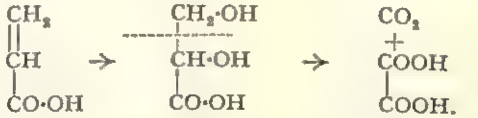
$$\underset{\text{Hydracrylic acid.}}{CH_2OH{\cdot}CH_2{\cdot}COOH} = \underset{\text{Acrylic acid.}}{CH_2{:}CH{\cdot}COOH} + H_2O.$$

Acrylic acid is a liquid with a pungent smell which boils at 140°. It possesses the properties of an unsaturated compound. On reduction, it yields propionic acid; with bromine it forms dibromopropionic acid; with hydrochloric acid it gives β-chloropropionic acid. In the latter case it should be noted that the halogen attaches itself to the carbon farthest from the carboxyl, which is the general rule when halogen acids unite with unsaturated acids—

$$\underset{\text{Dibromopropionic acid.}}{CH_2Br{\cdot}CHBr{\cdot}CO{\cdot}OH.} \qquad \underset{\beta\text{-Chloropropionic acid.}}{CH_2Cl{\cdot}CH_2{\cdot}COOH.}$$

When acrylic acid is oxidised with permanganate, dihydroxy-

propionic acid (glyceric acid) is first formed, which on further oxidation breaks up into carbon dioxide and oxalic acid—



Acrylic acid. Glyceric acid. Oxalic acid and Carbon dioxide.

Crotonaldehyde and *Crotonic Acid* are the next homologues of acrolein and acrylic acid.

Crotonaldehyde, $CH_3{\cdot}CH{:}CH{\cdot}CHO$, is prepared by heating acetaldehyde with zinc chloride. Aldol (p. 134) is first formed, which then loses a molecule of water—

$$\underset{\text{Aldol.}}{CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO} = \underset{\text{Crotonaldehyde.}}{CH_3{\cdot}CH{:}CH{\cdot}CHO} + H_2O.$$

Crotonaldehyde is a liquid which boils at 104°.

Crotonic Acid, $CH_3{\cdot}CH{:}CH{\cdot}COOH$, is obtained by the oxidation of crotonaldehyde; also by the hydrolysis of allyl cyanide and by the action of alcoholic potash on α-bromobutyric acid. Crotonic acid is a solid which melts at 72° and closely resembles acrylic acid in its chemical characters. It derives its name from *croton oil*, from which it was originally obtained. An isomeric acid, known as *isocrotonic acid*, has many of the properties of crotonic acid, but is a liquid at the ordinary temperature.

For an explanation of the isomerism of these two acids and also of oleic and elaidic acids (see below) the reader is referred to p. 366.

Oleic Acid, $C_{18}H_{34}O_2$, has already been referred to under fats and oils (p. 167); but belongs strictly to the acrylic acid series. In animal fat, olive oil and other vegetable oils, it is present as the glyceride or olein. Its lead salt is soluble in ether, and this property is utilised for separating it from stearic and palmitic acids, the lead salts of which are insoluble. Its relationship to stearic and palmitic acids as well as its unsaturated character are clearly exhibited by the following reactions. It forms additive compounds with iodine, bromine, and also with strong sulphuric acid.—

EXPT. 103.—Add a few drops of a solution of bromine in carbon tetrachloride to oleic acid or olein and shake up. The colour is at once discharged.

It is oxidised by fusion with caustic potash to palmitic acid and acetic acid—

$$\underset{\text{Oleic acid.}}{C_{18}H_{34}O_2} + H_2 = \underset{\text{Stearic acid.}}{C_{18}H_{36}O_2}.$$

$$C_{18}H_{34}O_2 + 2KOH = \underset{\substack{\text{Potassium}\\ \text{palmitate.}}}{C_{16}H_{31}O_2K} + C_2H_3O_2K + H_2.$$

It can also be reduced by hydrogen at 200°–250° in presence of finely divided nickel to stearic acid. Olein in the same way and many other liquid fats and oils are rendered solid (fat-hardening process).

When the compound with sulphuric acid is distilled with steam, it is converted into a solid isomer of oleic acid, known as *isoleic acid*, which can be used like stearic and palmitic acids in candle-making. This constitutes one of the advantages of the sulphuric acid saponification process (p. 168), as by this means a larger output of solid acids is obtained than by the other saponification methods. Another solid isomer, *elaidic acid*, is obtained by treating oleic acid with nitrous acid.

EXPT. 104.—Pour a few c.c. of oleic acid into a test-tube and add a small piece of sodium nitrite and a drop or two of strong nitric acid. Nitrous acid is evolved, and in a few minutes the oleic acid is converted into solid elaidic acid. A similar change occurs with olive oil.

The formation of these isomers may be explained either by a change produced in the position of the double bond in the chain of carbon atoms or by some difference in the space arrangement of the atoms; but these points will be more fully discussed in a subsequent chapter (p. 366).

Linoleic Acid, $C_{18}H_{32}O_2$, is present as the glyceride, together with the glycerides of linolenic acid, $C_{18}H_{30}O_2$, and other unsaturated acids, in the so-called *drying oils*, *e.g.*, linseed, cotton-seed, and rape-seed oils. These oils possess the property of absorbing oxygen from the air and changing into transparent resinous substances. The change is hastened by heating the oil with certain metallic compounds known as *driers*, such as lead oxide, manganese borate, etc. When linseed oil is thus treated it is known as *boiled linseed oil*.

Linseed Oil.—The boiled oil is used as a vehicle for pigments, and forms, when dry, a hard, protective, and at the same time trans-

parent, covering. By pouring successive layers of the oil on to cloth or canvas and freely exposing them to the air, the oil hardens and forms the material known as *oil-cloth*. *Linoleum* is produced in a similar manner by first oxidising the heated oil by blowing a current of air or oxygen through the liquid, thereby forcing it into a fine spray. The semi-solid gelatinous product is melted and mixed with powdered cork and other materials, and spread out in thin layers, which on cooling become solid.

The absorption of oxygen by drying oils is generally accompanied by a considerable rise of temperature, and fires have been known to originate through the spontaneous ignition of cotton waste which has become impregnated with oil in the cleaning of machinery.

Varnishes are also made from boiled linseed oil, by mixing it with certain gums or resins and diluting with turpentine or spirits of wine.

Ricinoleic Acid, $C_{18}H_{34}O_3$, is an unsaturated hydroxy-acid, *i.e.*, an unsaturated acid, which contains a hydroxyl group. It does not therefore belong to the acrylic series; but it is convenient to consider it here. It is present as the glyceride in *castor oil*; the latter being expressed from the seeds of the castor oil plant (*Ricinus*). When castor oil is mixed with strong sulphuric acid, it forms a compound which emulsifies in water, and after neutralising with alkali is used in dyeing, under the name of *Turkey red oil*.

The quantity of the glycerides of unsaturated acids present in various oils is estimated by the amount of iodine with which they combine, which is measured by adding a standard solution of iodine and estimating the quantity absorbed. The measure of this amount is known as the *iodine value* (p. 168).

Questions on Chapter XVIII

1. Why is allyl alcohol termed an *unsaturated primary alcohol?* How is it prepared?

2. How do you explain the difference in the formation of (1) formic acid and (2) allyl alcohol from glycerol and oxalic acid?

3. Describe the preparation of allyl iodide from glycerol. What other substance is obtained by the use of the same reagents?

4. What are *oil of mustard* and *oil of garlic?* What are the natural sources of these compounds, and how have they been synthesised?

5. How can oleic acid be obtained free from palmitic and stearic acids? What relation exists between these three acids?

6. Describe the preparation of acrolein. In what respects may it be said to possess mixed functions?

7. Describe and explain the technical uses of linseed oil.

8. Give an account of the action of chlorine, hydriodic acid, reducing and oxidising agents upon acrylic acid. How is it prepared?

9. Which classes of carbon compounds form "addition-products," and which of these classes would be termed unsaturated?

10. Describe the method by which oil of mustard can be formed from allyl iodide. Explain the action of ammonia on mustard oil.

11. Write the equations showing the conversion of glycerol into acrolein and acrolein into acrylic acid.

CHAPTER XIX

THE POLYHYDRIC ALCOHOLS AND THEIR DERIVATIVES

The Polyhydric Alcohols are, like methyl and ethyl alcohol, hydroxy-derivatives of the paraffins, but contain more than one hydroxyl group. According to the number of hydroxyl groups present in the compound, they are known as mono-, di-, tri-, etc., hydric alcohols. The names of all the alcohols terminate in the syllable *ol.* Thus ethyl alcohol, $C_2H_5{\cdot}OH$, is a monohydric alcohol; *glycol,* $C_2H_4(OH)_2$, a dihydric alcohol; *glycerol,* $C_3H_5(OH)_3$, a trihydric alcohol; *erythritol,* $C_4H_6(OH)_4$, a tetrahydric alcohol, and so forth. The properties of the hydroxyl group, which distinguish the monohydric alcohols as a class, are exhibited by all the polyhydric alcohols, but as the latter contain more than one hydroxyl group, and as each group retains its alcoholic characters, a much greater variety of products is necessarily formed by the action of reagents.

The Glycols, $C_nH_{2n}(OH)_2$, are so named from the first member, $C_2H_4(OH)_2$, now known as **ethylene glycol,** which was prepared in 1859 by Wurtz, and which like most of the glycols possesses a sweet taste (γλυκύς, sweet). The glycols are most easily prepared from the dihalogen derivatives of the paraffins by the action of water and metallic oxides, in much the same way as the monohydric alcohols are obtained from the alkyl halides (p. 83). Ethylene bromide, when boiled with water and potassium carbonate, yields ethylene glycol. The product is then distilled and fractionated—

$$\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} + H_2O + K_2CO_3 = \underset{\text{Ethylene glycol.}}{\begin{array}{l}CH_2{\cdot}OH\\ |\\ CH_2{\cdot}OH\end{array}} + 2KBr + CO_2.$$

Ethylene glycol made by a similar process from ethylene chloride (the ethylene being obtained from natural gas) is now a com-

5. How can oleic acid be obtained free from palmitic and stearic acids? What relation exists between these three acids?

6. Describe the preparation of acrolein. In what respects may it be said to possess mixed functions?

7. Describe and explain the technical uses of linseed oil.

8. Give an account of the action of chlorine, hydriodic acid, reducing and oxidising agents upon acrylic acid. How is it prepared?

9. Which classes of carbon compounds form "addition-products," and which of these classes would be termed unsaturated?

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CHAPTER XIX

THE POLYHYDRIC ALCOHOLS AND THEIR DERIVATIVES

The Polyhydric Alcohols are, like methyl and ethyl alcohol, hydroxy-derivatives of the paraffins, but contain more than one hydroxyl group. According to the number of hydroxyl groups present in the compound, they are known as mono-, di-, tri-, etc., hydric alcohols. The names of all the alcohols terminate in the syllable *ol*. Thus ethyl alcohol, $C_2H_5{\cdot}OH$, is a monohydric alcohol; *glycol*, $C_2H_4(OH)_2$, a dihydric alcohol; *glycerol*, $C_3H_5(OH)_3$, a trihydric alcohol; *erythritol*, $C_4H_6(OH)_4$, a tetrahydric alcohol, and so forth. The properties of the hydroxyl group, which distinguish the monohydric alcohols as a class, are exhibited by all the polyhydric alcohols, but as the latter contain more than one hydroxyl group, and as each group retains its alcoholic characters, a much greater variety of products is necessarily formed by the action of reagents.

The Glycols, $C_nH_{2n}(OH)_2$, are so named from the first member, $C_2H_4(OH)_2$, now known as **ethylene glycol,** which was prepared in 1859 by Wurtz, and which like most of the glycols possesses a sweet taste (γλυκύς, sweet). The glycols are most easily prepared from the dihalogen derivatives of the paraffins by the action of water and metallic oxides, in much the same way as the monohydric alcohols are obtained from the alkyl halides (p. 83). Ethylene bromide, when boiled with water and potassium carbonate, yields ethylene glycol. The product is then distilled and fractionated—

$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + H_2O + K_2CO_3 = \underset{\text{Ethylene glycol.}}{\begin{matrix} CH_2{\cdot}OH \\ | \\ CH_2{\cdot}OH \end{matrix}} + 2KBr + CO_2.$$

Ethylene glycol made by a similar process from ethylene chloride (the ethylene being obtained from natural gas) is now a com-

mercial product and can replace glycerol in many of its applications, whilst the ethers have been introduced as solvents.

Another method, which has already been mentioned, but is less common, is to oxidise the olefines with permanganate (p. 249). Neither methylene glycol, $CH_2(OH)_2$, ethylidene glycol, $CH_3 \cdot CH(OH)_2$, nor, in fact, any dihydric alcohol with both hydroxyls linked to one carbon atom is known in the free state. This is due to the instability of these compounds, which, by the removal of the elements of water, form aldehydes. This has already been explained on p. 88. Chloralhydrate appears to form an exception, and must be regarded as a trichlorethylidene glycol (p. 142). Although ethylidene glycol and its homologues are unknown, many of their derivatives have been obtained. The ethers of these compounds have already been described under the name of acetals (p. 134).

The glycols are colourless, rather viscid liquids resembling glycerol, with a high boiling-point and a sweet taste. They are very soluble in water.

Both the solubility in water and the high boiling-point must be ascribed to the presence of hydroxyl groups. Ethyl alcohol boils at 78°, whereas ethylene glycol boils at 195°.

The glycols exhibit all the properties of alcohols, but in a two-fold degree. Ethylene glycol is a di-primary alcohol, and by successive oxidation of the two carbinol groups to aldehyde and carboxyl groups the following series of products should be obtainable—

CH_2OH	CH_2OH	CHO	CHO	$CO \cdot OH$
$\vert$	$\vert$	$\vert$	$\vert$	$\vert$
CHO	$COOH$	CHO	$CO \cdot OH$	$CO \cdot OH$
Glycollic aldehyde.	Glycollic acid.	Glyoxal.	Glyoxalic acid.	Oxalic acid.

All these compounds are known, but only three of them, viz. glycollic, glyoxalic, and oxalic acid, have been directly obtained from glycol by oxidation. In regard to the action of other reagents on glycol, metallic sodium forms a mono- and di-sodium derivative; two sets of ethers are produced by the action of alkyl iodides on the sodium compounds, whilst two series of esters are obtained by the action of one or two molecules of acid chloride

on the glycol. The following are the compounds formed from ethylene glycol—

$$\begin{array}{ccc} \begin{array}{l} CH_2ONa \\ | \\ CH_2OH \end{array} & \begin{array}{l} CH_2{\cdot}OC_2H_5 \\ | \\ CH_2OH \end{array} & \begin{array}{l} CH_2{\cdot}OCO{\cdot}CH_3 \\ | \\ CH_2OH \end{array} \\ \text{Sodium glycolate.} & \text{Glycol ethyl ether.} & \text{Glycol monoacetate.} \\ \begin{array}{l} CH_2ONa \\ | \\ CH_2ONa \end{array} & \begin{array}{l} CH_2{\cdot}OC_2H_5 \\ | \\ CH_2{\cdot}OC_2H_5 \end{array} & \begin{array}{l} CH_2{\cdot}O{\cdot}CO{\cdot}CH_3 \\ | \\ CH_2{\cdot}O{\cdot}CO{\cdot}CH_3. \end{array} \\ \text{Disodium glycolate.} & \text{Glycol diethyl ether.} & \text{Glycol diacetate.} \end{array}$$

When hydrochloric acid gas is passed into a glycol, only one hydroxyl is replaced by chlorine, and the compounds which are thus obtained are identical with the chlorhydrins formed by the action of hypochlorous acid on the olefines (p. 249). Phosphorus chloride and bromide replace both hydroxyls by halogens, and form respectively ethylene chloride and bromide—

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + HCl = \underset{\text{Ethylene chlorhydrin.}}{\begin{array}{l} CH_2Cl \\ | \\ CH_2OH \end{array}} + H_2O.$$

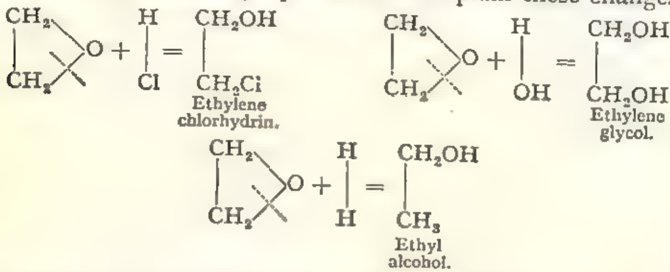
$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2PCl_5 = \underset{\text{Ethylene chloride.}}{\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}} + 2POCl_3 + 2HCl.$$

Ethylene Oxide, C_2H_4O.—By the action of caustic alkalis on the chlorhydrins, hydrochloric acid is removed and *alkylene oxides* are formed. Ethylene chlorhydrin yields ethylene oxide—

$$\begin{array}{l} CH_2 \quad Cl \\ | \\ CH_2O \quad H \end{array} + KOH = \underset{\text{Ethylene oxide.}}{O\begin{array}{l} \diagup CH_2 \\ \quad | \\ \diagdown CH_2 \end{array}} + KCl + H_2O.$$

It is isomeric with acetaldehyde and is an ethereal-smelling mobile liquid which boils at 14°. Ethylene oxide reacts with aqueous ammonia to form the basic alcohols, **ethanolamine,** $HO{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, **diethanolamine** $(HO{\cdot}CH_2{\cdot}CH_2)_2NH$, and **triethanolamine** $(HO{\cdot}CH_2{\cdot}CH_2)_3N$, the last of which is used in combination with fatty acids as an emulsifier. Although saturated ethylene oxide readily unites with halogen acids, water, nascent hydrogen,

and many reagents whereby one link between oxygen and carbon is broken. The following equations will explain these changes—



The affinity of ethylene oxide for hydrochloric acid is so great that it takes up the acid from solutions of metallic chlorides and precipitates the base. The same properties are exhibited by other alkylene oxides.

Diethylene dioxide, or Dioxan, $\begin{array}{l} CH_2—O—CH_2 \\ | \qquad\qquad\; | \\ CH_2—O—CH_2 \end{array}$, results from the condensation of ethyleneglycol and concentrated sulphuric acid. It melts at 11° C. and mixes with water and with organic solvents. It is a useful solvent for the cryoscopic determination of molecular weights, but its vapour is poisonous.

Sulphonal, $(CH_3)_2C(SO_2C_2H_5)_2$.—The acetals are formed, as we have seen, by the action of aldehydes on alcohols (p. 134). Aldehydes and ketones behave similarly with mercaptans. Thus, acetone and ethyl mercaptan react in presence of hydrochloric acid or zinc chloride and form a *mercaptol*—

$$\begin{array}{l} CH_3 \\ | \\ CO + \begin{array}{l} H\,SC_2H_5 \\ H\,SC_2H_5 \end{array} \\ | \\ CH_3 \end{array} = \begin{array}{l} CH_3 \\ | \\ C(SC_2H_5)_2 \\ | \\ CH_3 \end{array} + H_2O.$$

Mercaptol.

The latter when oxidised with permanganate solution yields sulphonal, which is largely used in medicine as a soporific (see p. 197).

Trional $(CH_3)(C_2H_5)C(SO_2C_2H_5)_2$, which is used for the same purpose, is obtained from methyl ethyl ketone $CH_3{\cdot}CO{\cdot}C_2H_5$, and *tetronal* is the tetraethyl derivative, $(C_2H_5)_2C(SO_2C_2H_5)_2$.

$$\begin{array}{l} CH_3 \\ | \\ C(SC_2H_5)_2 \\ | \\ CH_3 \end{array} + 2O_2 = \begin{array}{l} CH_3 \\ | \\ C(SO_2C_2H_5)_2. \\ | \\ CH_3 \end{array}$$

Sulphonal.

Glycerol, *Glycerine,* or *Glyceryl alcohol,*[1] $C_3H_5(OH)_3$, was discovered by Scheele in 1779, who found a sweet-tasting liquid separated when olive oil was heated with litharge. It was afterwards observed by Chevreul to be a common constituent of natural fats and oils (p. 166). The latter are still the chief source of glycerol. A small quantity of glycerol is always found among the products of alcoholic fermentation (p. 105). By the addition of sodium or calcium sulphite to the fermenting liquid the quantity of glycerol may be so largely increased as to become a commercial source of the material. Under these conditions the other chief product is not alcohol but acetaldehyde, which forms a bisulphite compound with the sodium sulphite. In this case the break up of glucose may be represented by the equation—

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = \underset{\text{Acetaldehyde.}}{CH_3{\cdot}CHO} + \underset{\text{Glycerol.}}{C_3H_8O_3} + CO_2.$$

Glycerol is a viscid, colourless liquid with a sweet taste, which, when pure, crystallises slowly on cooling and then melts at 17°. It boils at 290° with very slight decomposition when pure, and it can be readily distilled with superheated steam or under diminished pressure. It is hygroscopic and mixes with water in all proportions.

The constitution of glycerol has been determined by numerous syntheses. Acetone gives isopropyl alcohol on reduction, and the latter when heated with sulphuric acid forms propylene. Propylene combines with chlorine, giving propylene chloride, which iodine chloride converts into trichloropropane or glyceryl trichloride. When glyceryl chloride is heated with water to 170° it yields glycerol—

$$\begin{array}{ccccccc}
CH_3 & & CH_3 & & CH_2Cl & & CH_2(OH) \\
| & & | & & | & & | \\
CH & \xrightarrow{Cl_2} & CHCl & \xrightarrow{ICl} & CHCl & \xrightarrow{3H_2O} & CH(OH) \\
\| & & | & & | & & | \\
CH_2 & & CH_2Cl & & CH_2Cl & & CH_2(OH). \\
\text{Propylene.} & & \text{Propylene chloride.} & & \text{Glyceryl trichloride.} & & \text{Glycerol.}
\end{array}$$

Dihydroxyacetone, $CH_2OH{\cdot}CO{\cdot}CH_2OH$, has been obtained synthetically, and gives glycerol on reduction. Allyl alcohol can also be converted into glycerol by oxidation with permanganate.

[1] The term *glyceryl* is applied to the tervalent radical, $CH_2'{\cdot}CH'{\cdot}CH_2'$.

Chemical Properties of Glycerol.—The chemical behaviour of glycerol fully bears out the above constitution. It has the properties of a trihydric alcohol. Thus, mono-, di-, and tri-formyl and acetyl esters are known, which are named respectively mono-, di-, and tri-formin and acetin.

$$\begin{array}{lll} CH_2\cdot O\cdot CO\cdot CH_3 & CH_2\cdot O\cdot CO\cdot CH_3 & CH_2\cdot O\cdot CO\cdot CH_3 \\ | & | & | \\ CHOH & CH\cdot O\cdot CO\cdot CH_3 & CH\cdot O\cdot CO\cdot CH_3 \\ | & | & | \\ CH_2OH & CH_2OH & CH_2\cdot O\cdot CO\cdot CH_3 \\ \text{Mono-acetin.} & \text{Di-acetin.} & \text{Tri-acetin.} \end{array}$$

The glycerides of palmitic, stearic, and oleic acids, which occur in fats, etc., are triacid esters, and should strictly be termed tripalmitin, tristearin, and triolein.

The mono-, di-, and tri-nitrates of glycerol are also known, the latter being incorrectly named nitroglycerine (p. 283).

When hydrochloric acid gas is passed into glycerol it is absorbed and forms glycerol α-monochlorhydrin; if the glycerol is dissolved in acetic acid and heated whilst the gas is passed in, then the dichlorhydrin is produced; the third hydroxyl group can be replaced by chlorine by the action of phosphorus chloride, the product being glyceryl trichloride, which smells like chloroform. All three substances are liquids.

$$\begin{array}{ccc} CH_2OH & CH_2Cl & CH_2Cl \\ | & | & | \\ CHOH & CHOH & CHCl \\ | & | & | \\ CH_2Cl & CH_2Cl & CH_2Cl. \\ \text{Glycerol} & \text{Glycerol} & \text{Glyceryl} \\ \alpha\text{-monochlorhydrin.} & \alpha\alpha'\text{-dichlorhydrin.} & \text{trichloride.} \end{array}$$

Glycerol β-monochlorhydrin and glycerol αβ-dichlorhydrin are obtained from allyl alcohol by addition of hypochlorous acid and chlorine, respectively—

$$CH_2{:}CH\cdot CH_2OH + HOCl = \underset{\text{Glycerol }\beta\text{-chlorhydrin.}}{CH_2OH\cdot CHCl\cdot CH_2OH}$$

$$CH_2{:}CH\cdot CH_2OH + Cl_2 = \underset{\text{Glycerol }\alpha\beta\text{-dichlorhydrin.}}{CH_2Cl\cdot CHCl\cdot CH_2OH}$$

Both αα- and αβ-dichlorhydrins are decomposed by caustic alkalis to give a ring compound *epi*-**chlorhydrin**,

$$\begin{array}{c} CH_2Cl\cdot CH\cdot CH_2. \\ \diagdown\;\diagup \\ O \end{array}$$

The products of oxidation of glycerol, which are theoretically possible, are very numerous, and many of them have been obtained either directly or indirectly from glycerol. Glycerol contains two primary and one secondary alcohol group. The two primary groups should yield successively aldehyde and carboxyl groups; the secondary, a ketone group. By the action of dilute nitric acid on glycerol, glyceric and tartronic acids have been obtained. On further oxidation oxalic is formed.

$$\begin{array}{ccc} CH_2OH & \qquad & CO{\cdot}OH \\ | & & | \\ CHOH & & CH{\cdot}OH \\ | & & | \\ CO{\cdot}OH & & CO{\cdot}OH. \\ \text{Glyceric acid.} & & \text{Tartronic acid.} \end{array}$$

By the action of bromine in presence of sodium carbonate solution dihydroxyacetone is produced. A solution of caustic soda converts a part of the dihydroxyacetone into the isomeric compound glyceric aldehyde, and at the same time the alkali brings about the *aldol* condensation (p. 141) between the two molecules with the formation of an artificial sugar, which has been identified as inactive fruit sugar, α-acrose, or fructose (p. 297).—

$$\begin{array}{ccccccc} CH_2OH & & CH_2OH & & CH_2OH & & CH_2OH \\ | & & | & & | & & | \\ CHOH & + & CO & = & CHOH & & CO \\ | & & | & & | & & | \\ CHO & & CH_2OH & & CHOH & \text{———} & CHOH. \\ \text{Glyceric aldehyde.} & & \text{Dihydroxyacetone.} & & \text{Fructose, or } \alpha\text{-Acrose.} & & \end{array}$$

Glycerol undergoes fermentation with different ferments and gives rises to various products. Certain bacteria produce butyl alcohol, others ethyl alcohol, a third kind convert glycerol into dihydroxyacetone, etc.

Before discussing the industrial preparations and uses of glycerol the student is reminded of the various reactions already described in which glycerol plays a part.

Summary of Preparations in which Glycerol is used.—By distilling glycerol with potassium bisulphate, acrolein is formed (p. 269). By heating glycerol with oxalic acid, either formic acid (p. 158) or allyl alcohol (p. 268) is produced. By the action of phosphorus and iodine, isopropyl iodide (p. 85), allyl iodide (p. 267), or propylene is formed, according to the conditions of the reaction.

Manufacture of Glycerol.—Glycerol is manufactured on a large scale for a great variety of industrial purposes. The chief sources are the fats and oils and spent lyes of the soap-works. It has already been stated (p. 168) that the fats and oils are usually hydrolysed either with a little strong sulphuric acid or by superheated steam, in the presence of a small quantity of lime. In the sulphuric acid process, which is used for the poorer qualities of fat and oil, some of the glycerol is decomposed by the acid, but the remainder is recovered from the liquors from which the fatty acids have been separated. In the lime process, the "sweet water" which contains the glycerol is concentrated, filtered through animal charcoal to remove colouring matter, and evaporated to the requisite specific gravity. The spent lyes of the soap-works, containing 5 to 8 per cent. of glycerol, were until recently a waste-product. At the present time they are the main source of the glycerol used in commerce. The lyes contain large quantities of sodium chloride, free alkali, and fatty and resinous matters, which have first to be separated. The lyes are acidified, and filtered from the fatty and resinous matters, then neutralized and concentrated under diminished pressure, whereby the salts are deposited and removed. By whichever process the glycerol is obtained, it is usually purified by distillation with superheated steam. The distillate, which contains water, is evaporated to the requisite consistency in steam-heated vacuum pans, *i.e.*, vessels from which the air is partially exhausted (see p. 302). In this way evaporation can be rapidly effected at a temperature at which no decomposition or discoloration of the glycerol can occur. Glycerol combines with metaphosphoric acid to form glycerophosphoric acid—

$$C_3H_5(OH)_3 + HPO_3 = C_3H_5(OH)_2O{\cdot}OP(OH)_2,$$

the alkali salts of which are used as a tonic in medicine. Glycerol is used in the preparation of copying inks and of water-colour pigments. It is also added in small quantities to water in gas-meters and motor radiators to prevent freezing and enters into the composition of shoe polishes and soaps; But the greater part of the distilled glycerol is used in the manufacture of nitroglycerine.

Owing to the great demand for glycerol for the manufacture of explosives, other methods of manufacture have been developed.

When the fats are hydrolysed by steam under pressure at 120°–140° C. the glycerol concentration in the liquor is much higher than is the case with alkaline hydrolysis; or the hydrolysis is effected by using a catalyst, such as the enzyme *lipase*, or Twitchell's reagent, which is made by sulphonating a mixture of oleic acid and naphthalene. Another important source of glycerol is the hydrocarbon propylene, which is a by-product in the cracking of petroleum. By chlorinating propylene at high temperature, substitution takes place instead of addition, the main product being allyl chloride, $CH_2Cl{\cdot}CH{:}CH_2$. This is combined with hypochlorous acid, and the product, when hydrolysed, yields glycerol.

Nitroglycerine, *Glyceryl trinitrate, Nobel's oil,* $C_3H_5(ONO_2)_3$.—The formation of nitroglycerine by the action of nitric acid on glycerol was discovered by Sobrero in 1846, but the practical application of this discovery to the manufacture of explosives is due to Nobel, a Swedish engineer (1862). Nitroglycerine is prepared by mixing 12 parts of fuming nitric acid and 20 parts of sulphuric acid and injecting into the well-cooled acid mixture a spray of glycerol (4 parts), which is forced in by a current of air—

$$C_3H_5(OH)_3 + 3HNO_3 = \underset{\substack{\text{Glyceryl nitrate, or} \\ \text{Nitroglycerine.}}}{C_3H_5(ONO_2)_3} + 3H_2O.$$

The sulphuric acid serves to unite with the water which is formed in the reaction. The mixture is allowed to stand, and the nitroglycerine, which forms a layer on the surface, is run into water, from which it separates as a heavy oil. It is well mixed with the water and then with a solution of sodium carbonate to remove all trace of acid, which, if present, renders the substance liable to decompose and explode. It is finally freed from water by filtering through flannel or felt covered with a layer of salt.

Properties of Nitroglycerine.—Nitroglycerine is a heavy, colourless liquid of specific gravity 1·6 which solidifies at 8°. It has a sweetish, burning taste, and is poisonous. In minute doses it is used in medicine. When spread in a thin layer over a large surface, it may be ignited without danger, and burns quietly; but when suddenly heated, it explodes like most of the nitric esters. A more violent explosion is produced by detonation.

The uncertainty which first attended the use of the oil as an explosive led to the discovery that the admixture of inert absorbent materials, whilst increasing the explosive force, rendered the nitroglycerine less sensitive and more easily manipulated.

Dynamite is made by mixing 3 parts of nitroglycerine with 1 part of *kieselguhr*, a fine siliceous earth which is very light and porous, and can absorb considerable quantities of nitroglycerine without becoming pasty. The mixture is moulded and compressed into cartridges and fired by a detonator (mercury fulminate). **Blasting gelatine** or **gelignite** is made by dissolving 7 parts of nitrated cellulose (p. 314) in 93 parts of nitroglycerine, and forms a solid translucent mass. **Cordite** is prepared from nitroglycerine (18 parts) and guncotton (73 parts) made into a pulp with acetone, to which a little vaseline is added. The pulp is squeezed through small holes into threads from which the acetone evaporates, and the threads are cut up and used for smokeless rifle cartridges. A great number of explosives are prepared containing nitroglycerine mixed with such substances as sawdust, charcoal, nitrates of potassium and ammonium, etc., and are known as *forcite, vulcan powder, lithofracteur*, etc.

The method of preparing nitroglycerine resembles the formation of ethyl nitrate from ethyl alcohol and nitric acid. Nitroglycerine is in fact an ester and not a nitro-compound, and like an ester it is hydrolysed by caustic alkalis—

$$C_3H_5(ONO_2)_3 + 3HOK = C_3H_5(OH)_3 + KNO_3.$$

The name nitroglycerine is therefore a misnomer, but it has become established through usage as the technical name of the compound.

Higher Polyhydric Alcohols.—The tetrahydric alcohol, **erythritol,** $C_4H_6(OH)_4$, is found in certain lichens both free and as an ester. **Arabitol** and **Xylitol,** $C_5H_7(OH)_5$, are both pentahydric alcohols, and are obtained by the reduction of the corresponding aldehydes, arabinose and xylose, the former being a constituent of gum arabic and the latter of wood-gum (p. 315). **Mannitol, Dulcitol,** and **Sorbitol,** $C_6H_8(OH)_6$, are isomeric hexahydric alcohols. They are all found in different species of ash. Mannitol is obtained from *manna*, the dried sap of an ash which grows in the East, and is also formed by the reduction of the sugars, mannose and fructose

(pp. 297, 300). Dulcitol is prepared in the same way from Madagascar manna and by the reduction of galactose (p. 299); whilst sorbitol is found in the berries of the mountain ash (*Sorbus*) and in the sap of many fruit trees. It is also formed by the reduction of glucose (p. 291). They are all solid, sweet, and very soluble in water.

The polyhydric alcohols resemble glycerol in forming acetyl and nitric esters, the latter being explosive substances. By the action of hydriodic acid, secondary iodides are formed corresponding to the formation of isopropyl iodide from glycerol. Mannitol, dulcitol, and sorbitol all give secondary hexyl iodide—

$$CH_3{\cdot}CHI{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3.$$

Secondary hexyl iodide.

This fact is important as showing that these three substances contain an unbranched chain of carbon atoms.

Questions on Chapter XIX

1. Give examples of di-, tri-, tetra-, penta-, and hexa-hydric alcohols.

2. How are the glycols obtained? Compare the physical and chemical properties of ethyl alcohol and ethylene glycol.

3. What is the action of water and a metallic oxide on ethylidene chloride? What relation do the *acetals* bear to the glycols?

4. Give a list of all the possible oxidation products of ethylene glycol. Which of these have been actually obtained from the glycol?

5. Explain why glycol is regarded as a di-primary alcohol.

6. What two compounds have the formula C_2H_4O? How are they obtained, and what are their characteristic properties?

7. Give the formulæ of dioxan and the ethanolamines. How are they prepared?

8. What are the chief sources of glycerol, and how is it obtained? Why is glycerol regarded as a trihydric alcohol?

9. Describe the action of (1) nitric, (2) oxalic, and (3) hydriodic acids on glycerol.

10. How has glycerol been obtained synthetically?

11. What is nitroglycerine and how is it obtained? Is the substance correctly described as a nitro-compound? Give your reasons.

12. Trace the successive steps by which ethylene can be made to afford glycol. Point out the chief characters of the glycols as a class.

13. Common alcohol is spoken of as a primary monohydric alcohol; explain the meaning of this designation.

14. How is ethylene oxide prepared, and by what properties and reactions is it distinguished from acetaldehyde?

15. How is glycerol obtained? Describe the action upon it of hydriodic acid, hydrochloric acid, oxalic acid, nitric acid, acetyl chloride. What substance is formed on heating glycerol?

16. What are the natural sources of glycerol, and how is it obtained on the industrial scale? How can it be shown that glycerol is a trihydric alcohol, and what products are obtainable by its oxidation?

17. Describe the two distinct methods by which oleic acid and glycerol may be prepared from olive oil.

CHAPTER XX

THE CARBOHYDRATES

The Carbohydrates.—The sugars, together with many related compounds, such as starch, cellulose, the gums, which are important products of plant life, are conveniently grouped, along with compounds of similar nature found in the animal kingdom, as *carbohydrates.* It is incorrect, however, to suppose that these substances are hydrates of carbon, although their composition in the majority of cases can be expressed by the general formula $C_x(H_2O)_y$. The simplest members of the whole group are *hydroxyaldehydes* or *hydroxyketones.* While behaving like aldehydes or ketones, they retain the properties of alcohols. Thus glycollic aldehyde, $CH_2OH{\cdot}CHO$, glyceric aldehyde, $CH_2OH{\cdot}CHOH{\cdot}CHO$, and dihydroxy-acetone, $CH_2OH{\cdot}CO{\cdot}CH_2OH$, are simple carbohydrates, although the number of carbon atoms in the molecule is generally much larger.

Nomenclature.—The members of these two groups of compounds are denoted by the termination *-ose,* the hydroxy-aldehydes being called **aldoses,** and the hydroxy-ketones **ketoses,** whilst the number of carbon atoms in the compound is indicated by prefixing the Greek numeral to the syllable *-ose.* Thus, glycollic aldehyde is an aldobiose, glyceric aldehyde an aldo-triose; whereas dihydroxyacetone is a keto-triose. The necessity for this system of nomenclature is apparent when dealing with the higher members of the series, each of which can exist in several isomeric forms. There are, for example, 2 possible aldo-trioses (glyceric aldehydes), 4 possible aldo-tetroses, 8 possible aldo-pentoses and 16 possible aldo-hexoses, every one of which is known (see p. 296). There are also aldo-heptoses, octoses, nonoses, and a decose, with 7, 8, 9, and 10 carbon atoms, as well as isomeric ketoses.

CHO	CHO	CHO
$\vert$	$\vert$	$\vert$
$(CH{\cdot}OH)_2$	$(CH{\cdot}OH)_3$	$(CH{\cdot}OH)_4$
$\vert$	$\vert$	$\vert$
$CH_2{\cdot}OH$	$CH_2{\cdot}OH$	$CH_2{\cdot}OH$
Aldo-tetrose.[1]	Aldo-pentose.	Aldo-hexose.

[1] The grouping $(CH{\cdot}OH)_2$ is an abbreviated form for
—CH·OH·CH·OH—.

The existence of the large number of isomers in the examples given above is due to the difference in space arrangement or configuration of the atoms, which is discussed in a later part of the chapter (p. 296).

The wide distribution of the carbohydrates, their extensive consumption as food, and their employment in various industries, as in the manufacture of fabrics and paper and in the production of alcohol, have given them an interest and importance possessed by few other groups of organic compounds.

Classification of the Carbohydrates.—The sugars are sweet, crystalline compounds, which may or may not be resolved by hydrolysis into simple carbohydrates. Starch and cellulose, on the other hand, are more complex in structure and are tasteless and insoluble in water, but they are closely related to the sugars.

Table XII. contains a list of the more important natural carbohydrates.

TABLE XII.

THE NATURAL CARBOHYDRATES.

The Sugars.		
Monosaccharides,	*Disaccharides,* $C_{12}H_{22}O_{11}$,	*Polysaccharides,* $(C_6H_{10}O_5)_n$,
Pentoses, $C_5H_{10}O_5$,	+ Cane-sugar, or Sucrose	+ Starch
+ Arabinose	+ Milk-sugar, or Lactose	+ Cellulose
+ Ribose	+ Malt-sugar, or Maltose	− Inulin
+ Xylose		+ Glycogen
Hexoses, $C_6H_{12}O_6$,	*Trisaccharide,* $C_{18}H_{32}O_{16}$,	+ Dextrin
+ Glucose, Grape-sugar, or Dextrose	+ Raffinose, or Melitriose	The Gums
− Fructose, Fruit-sugar, or Lævulose	*Tetrasaccharide,* $C_{24}H_{42}O_{21}$	
+ Galactose	+ Stachyose	
+ Mannose		

We can classify all the carbohydrates by reference to their behaviour towards hydrolytic reagents. Those which are not resolved by hydrolysis into simpler members are called *mono-*

saccharides, the most important of which are the pentoses, $C_5H_{10}O_5$, and the hexoses, $C_6H_{12}O_6$. *Disaccharides*, $C_{12}H_{22}O_{11}$, are hydrolysed to monosaccharides, each molecule uniting with one of water to produce two of a hexose; similarly *trisaccharides*, $C_{18}H_{32}O_{16}$, and *tetrasaccharides*, $C_{24}H_{42}O_{21}$, yield 3 and 4 hexose molecules respectively. Still more complex carbohydrates are the polysaccharides, with the empirical formula $(C_6H_{10}O_5)_x$, which can also be resolved into hexoses, but their molecular complexity is not yet known with certainty. Most of the soluble carbohydrates are optically active in solution. In the table the + and — signs signify dextro- and lævo-rotations respectively. In addition to these, many sugars have been synthesised.

The Monosaccharides

General Properties of the Monosaccharides.—The monosaccharides possess strong reducing properties, causing the separation of metallic silver from ammonia-silver-nitrate solution, and precipitating cuprous oxide from an alkaline solution of copper sulphate. They thus resemble aldehydes. Moreover, like aldehydes and ketones, they form cyanhydrins with hydrocyanic acid, oximes with hydroxylamine, and phenylhydrazones with phenylhydrazine (p. 131). The phenylhydrazones are, as a rule, very soluble in water; but, by the further action of phenylhydrazine, they are converted into insoluble yellow crystalline compounds known as *osazones*. The osazones are nearly insoluble in water, and readily separate from a solution containing the sugar. They have, moreover, a definite melting-point, and seen under the microscope possess a characteristic crystalline appearance. The reaction is therefore of considerable importance in detecting and identifying certain of the sugars. The monosaccharides are readily oxidised. The aldoses yield mono-and di-basic acids containing the same number of carbon atoms; the ketoses break up into acids with fewer carbon atoms. They all yield oxalic acid when warmed with strong nitric acid (p. 343). With strong hydrochloric acid they form levulinic acid (p. 331). Finally, they undergo alcoholic fermentation with yeast (p. 104). These reactions will be discussed in detail under glucose.

Glucose, Grape-Sugar, or **Dextrose,** is widely distributed among plants, especially in the sweet-tasting parts, as in the nectar of

flowers and in ripe fruit, where it is usually associated with fruit- and cane-sugar. It has received the name grape-sugar from its presence in ripe grapes, of dextrose from its dextro-rotation, and of glucose from its sweet taste (γλυκύς, sweet).

The discovery of a lævo-rotatory grape-sugar has led to the substitution of the name *dextro-glucose*, or simply glucose, for dextrose, although the latter name is still retained for the natural sugar. Glucose is a constituent of many glucosides (p. 212). In cases of *diabetes mellitus* it is found in the urine, sometimes to the extent of 8 to 10 per cent.

In small quantities pure glucose is most readily obtained from cane-sugar. Cane-sugar is dissolved in 90 per cent. alcohol and a little strong hydrochloric acid added. On gently warming the mixture, the cane-sugar is hydrolysed, and breaks up into glucose and fructose—

$$\underset{\text{Cane-sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Fructose.}}{C_6H_{12}O_6}.$$

Glucose, being less soluble in alcohol than fructose, separates in anhydrous crystals.

Glucose is manufactured by boiling starch with very dilute sulphuric acid. The starch is thereby hydrolysed and converted into glucose (p. 310). The liquid is neutralised with chalk and filtered, and the filtrate decolorised by filtration through animal charcoal. The solution is evaporated to the requisite consistency in vacuum-pans (p. 302). The product solidifies on cooling, and forms an amorphous-looking mass, which always contains dextrin (p. 311). Commercial glucose is used as a sweetening material in the manufacture of confectionery, preserved fruit and jam, wines, liqueurs, and as a substitute for malt in the brewing of beer.

Properties of Glucose.—Pure glucose dissolves in 1·2 parts of water. It crystallises from aqueous solution with 1 molecule of water, and the crystals melt at 86°, whilst from alcohol the anhydrous compound separates, melting at 146°. Glucose is dextro-rotatory in aqueous solution. When freshly dissolved in water it shows *a specific rotation* [1] of $[\alpha]_D^{20^\circ} = +110{\cdot}2^\circ$ which falls

[1] For *specific rotation*, see Chapter XXIII.

rapidly and then gradually more and more slowly until after the lapse of about 6 hours it reaches a constant value of $+52{\cdot}5^\circ$. This change of rotatory power is called **mutarotation** and is due to structural changes which occur in solution. Many other sugars undergo mutarotation. Another variety of glucose obtained by crystallisation from alcohol has a specific rotation of $+19^\circ$, a solution of which on standing rises to $+52{\cdot}5^\circ$. The two sugars are known as α- and β-glucose (p. 295) and the value $+52{\cdot}5^\circ$ is the specific rotatory power of an equilibrium mixture. In general the α-sugars are characterised by a *fall* and the β-sugars by a rise in the initial value of the rotation.

When lime or baryta solution is added to a solution of glucose, and then alcohol, glucosates of calcium or barium are precipitated. These compounds are soluble in water, and are decomposed by carbon dioxide into the original sugar and the carbonate of the metal. Calcium glucosate has the formula $C_6H_{12}O_6{\cdot}CaO$.

Glucose is converted, on oxidation, first into gluconic acid and then into saccharic acid. These two acids have the following formulæ—

$$\begin{array}{l}CH_2{\cdot}OH\\ \ |\\ (CH{\cdot}OH)_4\\ \ |\\ CO{\cdot}OH\end{array}\qquad\qquad\begin{array}{l}CO{\cdot}OH\\ \ |\\ (CH{\cdot}OH)_4\\ \ |\\ CO{\cdot}OH\end{array}$$

Gluconic acid. Saccharic acid.

Strong nitric acid converts glucose, as it does cane-sugar and the other carbohydrates, into oxalic acid (p. 343). By reducing glucose with sodium amalgam, sorbitol is formed (p. 284).

Reactions of Glucose.—Glucose gives the following series of reactions: Caustic alkalis, added to a solution of glucose and warmed, produce a brown solution.

Expt. 105.—Add a few drops of caustic soda solution to a dilute solution of glucose, and warm gently. The colour of the liquid changes to yellow and then to brown.

Glucose reduces an ammoniacal solution of silver oxide, metallic silver being deposited.

EXPT. 106.—Add a few drops of a solution of glucose to half a test-tube of ammonia-silver-nitrate solution, and heat the test-tube in hot water. A mirror of silver will be deposited.

The following reaction which is given by all soluble carbohydrates is known as *Molisch's test*.

EXPT. 107.—Add two or three drops of an alcoholic solution of α-naphthol to the glucose solution and carefully pour down the side of the test-tube some strong sulphuric acid. At the junction of the two layers a blue or violet colour will be developed.

An alkaline solution of copper sulphate is reduced, and cuprous oxide is precipitated.

EXPT. 108.—Add two or three drops of copper sulphate solution to a solution of glucose, and then caustic soda solution, until a clear blue solution is obtained. When the liquid is boiled, a yellow precipitate of cuprous oxide is formed, which rapidly turns red.

Analysis of Glucose.—The above reaction is utilised for the quantitative estimation of glucose as well as other sugars. A standard solution of copper sulphate is prepared by dissolving a carefully weighed quantity of the salt (34·64 grams) in a measured volume of water (500 c.c.). A second solution is prepared containing caustic soda (60 grams) and Rochelle salt (sodium potassium tartrate, 173 grams) in 500 c.c. of water. Equal volumes of the two solutions are mixed before use. This alkaline copper solution is known as *Fehling's Solution*. A measured volume of Fehling's solution is run into a flask and boiled, and the sugar solution is then added gradually from a burette until the whole of the copper is exactly precipitated as cuprous oxide. The quantity of sugar solution taken is a measure of the amount of glucose present. 10 c.c. of Fehling's solution corresponds to 0·05 gram of glucose.

Phenylhydrazine in presence of acetic acid produces, on heating, a yellow, crystalline precipitate of phenylglucosazone.

EXPT. 109.—Dissolve about 0·5 gram of glucose in 5 c.c. of water, and add a solution of phenylhydrazine acetate. The acetate is prepared by dissolving about 1 gram of phenylhydrazine in the same weight of glacial acetic acid and diluting to 10 c.c. Mix the two solutions in a test-tube and heat in boiling water. In a few minutes a yellow, crystalline mass of phenylglucosazone is deposited, seen under the microscope in the form of crystalline tufts. The substance melts

at 204–5°. The reaction occurs according to the following series of equations. Glucose phenylhydrazone is first formed—

$$\text{1. }\begin{array}{l} CH_2OH \\ | \\ (CH{\cdot}OH)_4 \\ | \\ CH\boxed{O + H_2}N{\cdot}NH{\cdot}C_6H_5 \end{array} = \begin{array}{l} CH_2{\cdot}OH \\ | \\ (CH{\cdot}OH)_4 \\ | \\ CH{:}N{\cdot}NHC_6H_5 \\ \text{Glucose phenylhydrazone.} \end{array} + H_2O.$$

The glucose phenylhydrazone is oxidised by a second molecule of phenylhydrazine and converted into a ketone, which is the phenylhydrazone of glucosone, and the latter unites with a third molecule of phenylhydrazine and forms the glucosazone—

$$\text{2. }\begin{array}{l} CH_2OH \\ | \\ (CH{\cdot}OH)_3 \\ | \\ CH{\cdot}OH \\ | \\ CH{:}N{\cdot}NH{\cdot}C_6H_5 \end{array} + NH_2{\cdot}NH{\cdot}C_6H_5 = \begin{array}{l} CH_2{\cdot}OH \\ | \\ (CH{\cdot}OH)_3 \\ | \\ CO \\ | \\ CH{:}N{\cdot}NHC_6H_5 \\ \text{Phenylhydrazone of glucosone.} \end{array} + NH_3 + \underset{\text{Aniline.}}{NH_2C_6H_5}.$$

$$\text{3. }\begin{array}{l} CH_2OH \\ | \\ (CH{\cdot}OH)_3 \\ | \\ C\boxed{O + H_2}N{\cdot}NHC_6H_5 \\ | \\ CH{:}N{\cdot}NHC_6H_5 \end{array} = \begin{array}{l} CH_2OH \\ | \\ (CH{\cdot}OH)_3 \\ | \\ C{:}N{\cdot}NH{\cdot}C_6H_5 \\ | \\ CH{:}N{\cdot}NHC_6H_5 \\ \text{Phenylglucosazone.} \end{array} + H_2O.$$

Conversion of Glucose into Fructose.—When phenylglucosazone is hydrolysed with hydrochloric acid, glucosone and phenylhydrazine are produced. When glucosone is reduced it yields fructose—

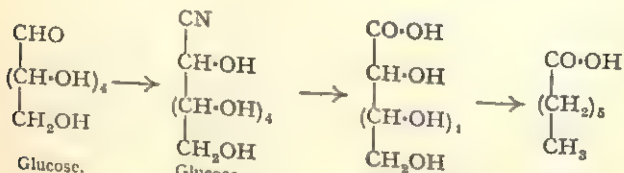
$$\text{4. }\begin{array}{l} CH_2OH \\ | \\ (CH{\cdot}OH)_3 \\ | \\ C{:}N{\cdot}NH{\cdot}C_6H_5 \\ | \\ CH{:}N{\cdot}NH{\cdot}C_6H_5 \end{array} + 2H_2O = \begin{array}{l} CH_2OH \\ | \\ (CH{\cdot}OH)_3 \\ | \\ CO \\ | \\ CHO \\ \text{Glucosone.} \end{array} + 2HN_2{\cdot}NH{\cdot}C_6H_5.$$

$$\text{5. }\begin{array}{l} CH_2OH \\ | \\ (CH{\cdot}OH)_3 \\ | \\ CO \\ | \\ CHO \end{array} + H_2 = \begin{array}{l} CH_2OH \\ | \\ (CH{\cdot}OH)_3 \\ | \\ CO \\ | \\ CH_2{\cdot}OH \\ \text{Fructose.} \end{array}$$

Fructose also reacts with phenylhydrazine, the keto-group being attacked first to give fructosephenylhydrazone, which is then oxidised to give another carbonyl group, which can react with more phenylhydrazine to give a phenylosazone (p. 297), which is identical with glucosazone. The fact that both sugars give the same osazone indicates that those parts of their molecules which are not concerned in osazone formation must have the same configuration.

Constitution of Glucose.—Glucose forms a pentacetyl derivative with acetic anhydride, and therefore contains 5 hydroxyl groups. Each hydroxyl group is probably attached to a different carbon atom, seeing that the attachment of 2 hydroxyl groups to the same carbon atom would form a very unstable arrangement (p. 89). The various reactions already described stamp glucose as an aldehyde. The only point which is left uncertain is whether or not the carbon atoms are in an unbranched chain. This point is determined by the reduction of glucose to sorbitol, and the conversion of the latter by means of hydriodic acid into *normal* secondary hexyl iodide (p. 285).

It has also been shown that glucose combines with hydrocyanic acid, and forms a cyanhydrin which, on hydrolysis, yields an acid. By the reduction of this acid with hydriodic acid, *normal* heptylic acid is produced. These changes are represented by the following formulæ—



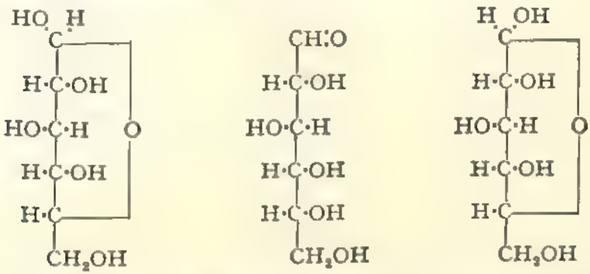
Glucose. Glucose cyanhydrin. Hydroxy-heptylic acid. Heptylic acid.

The formula for glucose would therefore appear to be a pentahydroxyaldehyde—

$$CH_2(OH) \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CHO.$$

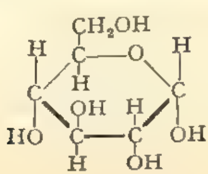
This formula does not, however, strictly conform to its behaviour; for a study of the two methyl glucosides (p. 212) has revealed the

fact that both glucose and the glucosides exist in cyclic forms. Since the terminal (aldehydic) group of glucose is involved in the ring formation, this carbon atom becomes asymmetric, and in this way gives rise to the stereoisomers α- and β-glucose and α- and β-glucosides. Further investigation has shown that the rings are 6-membered, with an oxygen atom linked to the first and fifth carbon atoms. But since glucose always reacts as if a carbonyl group were present, it can presumably isomerise easily to an open-chain structure. The α- and β-ring structures and the open-chain formula for glucose are as follows—



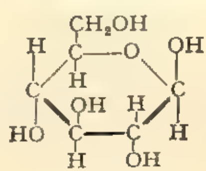
1.
2.
3.
4.
5.
6.

It is convenient to be able to refer to the different carbon atoms by means of numbers, which are indicated on the right-hand side. The two ring structures differ only in the disposition of the groups attached to No. 1 carbon atom. The configuration of the other four asymmetric carbon atoms (nos. 2, 3, 4, and 5) has been accurately determined, and is here indicated by means of projection formulæ (p. 367). Although these projection formulæ are quite satisfactory for open-chain compounds, some confusion is apt to arise whenever the chain is closed to a ring, so that Haworth has adopted the use of *perspective* formulæ, which reveal the ring as a hexagon, the groups attached to the carbon atoms being shown either above or below the plane of the hexagon, as the case may be, thus—



α-Glucopyranose.

and



β-Glucopyranose.

These are called **pyranose** forms. Other rings called **furanose** rings are formed with only four carbon atoms and one of oxygen. These terms are derived from *pyran* and *furan* (p. 563).

Since every asymmetric atom gives rise to two stereoisomers, every additional one of them must produce two more from each of these. Thus the aldopentoses with 3 asymmetric carbon atoms exist in 8 active forms, whilst the aldohexoses with 4 asymmetric atoms gives rise to 2 × 8 or 16, all of which are known. The most important of these are *d*-glucose, *d*-galactose, and *d*-mannose.

Fructose, Fruit-Sugar, or **Lævulose,** $C_6H_{12}O_6$.—It has already been stated that fruit-sugar is associated with grape-sugar in many fruits, and the mixture is probably produced by the hydrolysis of cane-sugar, which is now known to precede the formation of the other carbohydrates in plants. The name lævulose, which was given to the natural sugar on account of its lævo-rotation, has been replaced by the word fructose, since the discovery of a dextro-rotatory isomer. Fructose may be obtained from cane-sugar by hydrolysis with dilute sulphuric acid. The acid is removed by precipitation with barium carbonate, and the filtrate is concentrated. Milk of lime is then added, when the lime compound or calcium fructosate (corresponding to calcium glucosate, p. 291), which is only slightly soluble, separates out, and is filtered and washed. The calcium compound is then suspended in water and decomposed by carbon dioxide. The solution is again filtered from calcium carbonate and evaporated. On introducing a crystal of fructose into the syrup, the latter slowly crystallises. Fructose is prepared from inulin (p. 315) which is completely converted into fruit-sugar on hydrolysis with sulphuric acid. After removal of the acid, the liquid is evaporated, preferably under diminished pressure, when a syrup is left which solidifies if a crystal of the substance is added.

Fructose is now produced commercially for the use of diabetic patients to replace cane-sugar. It appears to be assimilated, whereas glucose is excreted unchanged. Fructose is more soluble than glucose but crystallises from alcohol in rhombic prisms which melt at 95°. It has a sweet taste and gives many of the reactions of glucose. Although fructose is not an aldehyde but a ketone (see below), it nevertheless reduces alkaline copper solution. This is

due to the presence of the easily oxidisable group $—CO·CH_2(OH)$. With phenylhydrazine, fructose yields an osazone, which is identical with glucosazone. Fructose also undergoes fermentation with yeast, though less readily than glucose, glucose being first removed when a solution of the two sugars is fermented. Like glucose, fructose undergoes mutarotation in solution, the specific rotation rising from $[\alpha]_D^{20^\circ} = -133{\cdot}5^\circ$ to $-92{\cdot}0^\circ$.

Constitution of Fructose.—Fructose forms a pentacetyl derivative, like glucose. On reduction, it is converted into a mixture of sorbitol and mannitol, since an additional asymmetric combination has been introduced. On oxidation, it does not, like glucose, form an acid with the same number of carbon atoms, but breaks up into formic acid and trihydroxybutyric acid. This decomposition points to the presence of a ketone group in the molecule (p. 127), which is further confirmed by the following reactions:—Fructose forms a cyanhydrin with hydrocyanic acid, which on hydrolysis yields an acid. The latter, on reduction with hydriodic acid, is converted into methylbutylacetic acid. The reactions are readily explained on the assumption that fructose is a hydroxyketone, in which the ketone group adjoins one of the end carbon atoms—

$$\begin{array}{c} CH_2{\cdot}OH \\ | \\ CO \\ | \\ (CH{\cdot}OH)_3 \\ | \\ CH_2{\cdot}OH \\ \text{Fructose.} \end{array} \longrightarrow \begin{array}{c} CH_2{\cdot}OH \\ | \\ C{<}^{OH}_{CN} \\ | \\ (CH{\cdot}OH)_3 \\ | \\ CH_2{\cdot}OH \\ \text{Cyanhydrin of fructose.} \end{array} \longrightarrow \begin{array}{c} CH_2{\cdot}OH \\ | \\ C{<}^{OH}_{COOH} \\ | \\ (CH{\cdot}OH)_3 \\ | \\ CH_2{\cdot}OH \\ \text{Hydroxy-acid.} \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ CH{\cdot}COOH \\ | \\ (CH_2)_3 \\ | \\ CH_3 \\ \text{Methylbutyl-acetic acid.} \end{array}$$

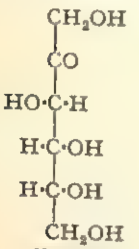
The above formula for fructose agrees, moreover, with the synthesis of inactive fructose from the mixture of glyceric aldehyde and dihydroxyacetone (p. 281), and with the production of the same osazone as that obtained from glucose, a reaction in which the two end carbon atoms of the chain are involved (p. 294)—

$$\begin{array}{l} CH_2OH \\ | \\ C\boxed{O + H_2}N{\cdot}NH{\cdot}C_6H_5 \\ | \\ (CH{\cdot}OH)_3 \\ | \\ CH_2OH \end{array} = \begin{array}{c} CH_2OH \\ | \\ C{:}N{\cdot}NH{\cdot}C_6H_5 \\ | \\ (CH{\cdot}OH)_3 \\ | \\ CH_2OH \\ \text{Fructose phenylhydrazone.} \end{array} + H_2O$$

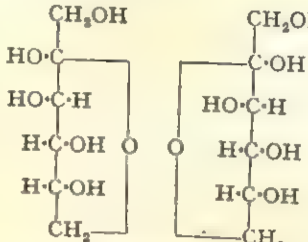
$$\begin{array}{l} CH_2OH \\ | \\ C{:}N{\cdot}NH{\cdot}C_6H_5 \\ | \\ (CH{\cdot}OH)_3 \\ | \\ CH_2OH \end{array} + 2C_6H_5NH{\cdot}NH_2 = \begin{array}{l} CH{:}N{\cdot}NH{\cdot}C_6H_5 \\ | \\ C{:}N{\cdot}NH{\cdot}C_6H_5 \\ | \\ (CH{\cdot}OH)_3 \\ | \\ CH_2OH \end{array} + C_6H_5NH_2 + NH_3.$$

Phenylglucosazone.

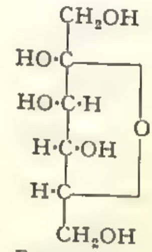
Although fructose in many of its reactions resembles a ketone, it exists like glucose in α- and β-stereoisomeric pyranose forms and also in γ- or furanose rings.



Keto formula fructose.

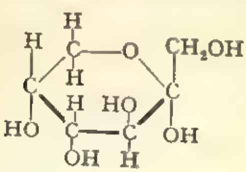


α- and β-Fructo-pyranose.

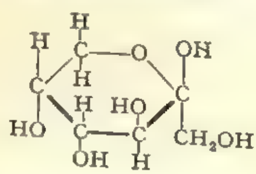


Fructo-furanose γ-fructose.

The perspective formulæ for α- and β-fructopyranose are



and



γ-Fructose is a constituent of cane-sugar (p. 306), but when liberated from its union with glucose passes into the pyranose form.

Nomenclature of the Sugars.—It should be noted that although fructose from the inversion of cane-sugar is lævo-rotatory, it is called *d*-fructose, on account of its close chemical relationship to *d*-glucose. Similar anomalies occur with other sugars. In spite of the confusion which arises in this way, the prefixes *d*- and *l*- in the sugar series all denote chemical relationship rather than the sign of the rotation, which is now indicated by using the symbols + and −. Thus ordinary glucose is *d*-(+)glucose, ordinary fructose is *d*-(−)fructose, its dextro-rotatory isomer being *l*-(+)-

fructose. The determination of structural differences in the molecules of sugars has been a formidable problem; yet much has been accomplished, and in many cases the actual configuration of all the groupings is known, but a discussion of the methods used is beyond the scope of this book. It should, however, be noted that the first important success in this direction was achieved by E. Fischer when he discovered the osazones. Sugars are often difficult to crystallise on account of the presence in the solutions of impurities or related compounds, but the osazones are readily purified by crystallisation, and are frequently used for the characterisation of sugars. It must be remembered, however, that the same osazone may result from different sugars, thus *d*-glucose, *d*-fructose, and *d*-mannose all give the same osazone. Glucosides and other ring compounds, which cannot exist in chain form, and do not therefore possess a "free carbonyl" group, do not yield osazones.

Galactose, $C_6H_{12}O_6$, is obtained from milk-sugar or lactose (p. 306) by boiling with dilute sulphuric acid. The milk-sugar decomposes into glucose and galactose in much the same way that cane-sugar yields glucose and fructose—

$$\underset{\text{Milk-sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Galactose.}}{C_6H_{12}O_6}.$$

To prepare galactose, milk-sugar is boiled with dilute sulphuric acid, the solution neutralised with baryta and concentrated by evaporation. On the introduction of a crystal of the pure compound, galactose crystallises out, and the crystals are purified by washing with dilute alcohol.

Galactose is less soluble in water than glucose or fructose. It crystallises in microscopic hexagonal plates melting at 68°. It forms a pentacetyl derivative. On reduction it yields dulcitol (p. 285), and on oxidation it forms the monobasic acid, *galactonic acid*, which is isomeric with gluconic acid, and the dibasic acid, *mucic acid*, which is isomeric with saccharic acid. It reduces alkaline copper sulphate solution, forms an osazone, which melts at 193°–194°, and undergoes fermentation by yeast, but more slowly than either glucose or fructose. The properties of galactose point to the same structural formula as that of glucose, and the difference between the two compounds must be one of space arrange-

ment or configuration of the atoms (p. 295). It is dextro-rotatory and shows mutarotation. $[\alpha]_D^{20°}$ falls from + 144° to + 80·5°.

Mannose, $C_6H_{12}O_6$, was first obtained by the oxidation of mannitol, with bromine in presence of sodium carbonate; but it has since been identified as one of the products of hydrolysis of certain carbohydrates, such as the cellular tissue of the *ivory-nut*. Mannose, unlike the other hexoses, forms an insoluble phenylhydrazone by which it may be identified. It is isomeric with glucose, and yields the same osazone, but possesses a different configuration. It is dextro-rotatory, and undergoes fermentation by yeast.

Sorbinose (*Sorbose*), $C_6H_{12}O_6$, is found in the juice of mountain-ash berries after standing, and is formed by the oxidation of sorbitol, which is always present in the berries, by the intervention of the *sorbose bacterium*. Sorbinose is a ketose, like fructose.

Disaccharides

Cane-Sugar (*Sucrose*), $C_{12}H_{22}O_{11}$, is found in the root, the tubers, and in the stems and flowers of many plants, as well as in the sap of certain trees. It is obtained chiefly from beet-root and sugar-cane; and in the United States, to a small extent, from the sugar maple, maize, and sorghum, a plant belonging to the grass family. Cane-sugar, known as *jaggery*, is made from a species of palm.

The sugar-cane was originally grown in the East—India and Arabia—and was introduced into Southern Europe by the Moors, whence it was transplanted to the West Indies and other tropical countries.

The Sugar-Cane Industry.—The sugar-cane contains 16–18 per cent. of cane-sugar. The canes are cut up and passed between hot rollers, whereby the juice is expressed. The extracted canes are known as *begasse*. The juice, which contains 19–20 per cent. of sugar, and small quantities of inorganic salts, organic acids, and albuminoid substances, is run directly into a copper vessel or *clarifier*, mixed with milk of lime, and boiled. The albuminoid substances are coagulated, and, together with the lime salts of the acids, form a scum on the surface, which is removed. The juice is further concentrated until the point of crystallisation is reached, when it is run into casks, the bottoms of which are pierced with holes through which the molasses, or treacle, drains, or the crystals are separated by a centrifugal machine. The raw, or Muscovado,

sugar is exported, and subsequently undergoes a process of refining, which is described further on.

The Beet-root Sugar Industry.—The presence of sugar in beet-root was observed in 1747 by the German chemist Marggraf, who suggested the cultivation of beet as a source of sugar; but the early attempts to utilise it commercially proved unprofitable. The success of the industry dates from about the year 1830, when important improvements began to be introduced. Careful selection of seed, and improved cultivation, nearly doubled the quantity of sugar in the beet. The use of steam-heated vacuum-pans gave a larger yield of crystallisable sugar, and new mechanical appliances for saving labour lowered the cost of production. Moreover, a method for revivifying the charcoal used for decolorising the raw sugar (after being used for a time it becomes inactive), and the introduction of a process for separating crystallised sugar from the molasses, combined to cheapen the product.

Beet-root contains about 13–14 per cent. of cane-sugar. The other solid constituents are a sugar known as *raffinose*, which subsequently remains in the molasses, small quantities of citric, oxalic, tannic, and tartaric acids, albumin, asparagine (p. 354), betaine (p. 325), etc. The roots are washed and rasped into very thin slices, and then macerated in warm water. The process of maceration is known as *diffusion*. It is in reality a process of dialysis, the cell-wall acting as a diaphragm through which the sugar and the other crystalline substances pass, whilst the albumin and non-crystalline contents of the cell are retained. The maceration is conducted in a series, or *battery*, of tanks containing the beet-root pulp, and filled up with hot water. The pulp in each tank is in a different stage of extraction, fresh pulp being at one end of the series and extracted pulp at the other. The water is pumped through the tanks in succession, so that fresh water comes in contact with the exhausted pulp, whilst the highly charged juice, which has passed through the tanks, is used for extracting the fresh beet. The juice, drawn from the tanks, is then heated with the addition of lime, which precipitates the acids and coagulates the albumin. Carbon dioxide is passed through the liquid to decompose the saccharosate of lime which is formed. The two processes, which are usually combined in one operation, are termed

respectively *defecation* and *saturation*. The operation is sometimes repeated, using sulphur dioxide in place of carbon dioxide to decolorise the juice. The mixture is now pumped through a filter-press to remove the insoluble substances, and the clear juice is evaporated in vacuum-pans, heated by steam from which the air is partially exhausted. A form of vacuum-pan is shown in section in Fig. 75. It consists of an iron pan, which is heated by vertical steam coils placed in the lower part of the vessel. Two or three pans are connected, so that the steam arising from the evaporation of the liquid in the first pan is utilised for heating the next, and its vapour passes on to the third. Between the pans a small cylindrical vessel is interposed, which serves to collect any juice which "primes," or is carried over during the boiling. The evaporation is continued until the liquid is so far concentrated that it shows "grain," or commences to crystallise. It is then run out and cooled, and the uncrystallisable portion, or molasses, separated in a centrifugal extractor.

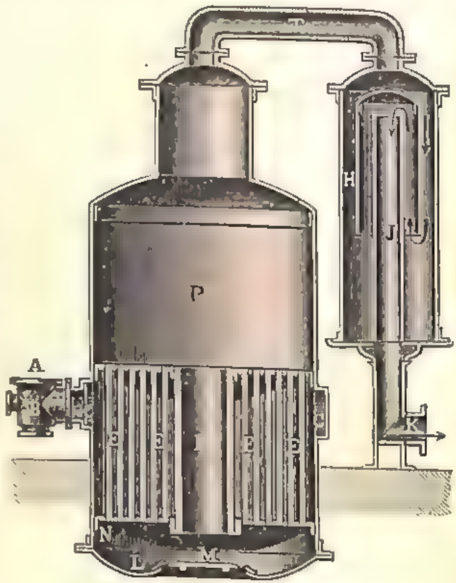


FIG 75.—Vacuum-pan.

Extraction of Sugar from Molasses.—The foreign substances in the molasses prevent its crystallisation. Among the numerous processes proposed for separating crystallisable sugar from molasses the *strontia method* is most commonly used. By this method nearly the whole of the cane-sugar is separated in the crystalline form. A hot saturated solution of strontium hydrate is added to the molasses, which, when excess of strontia is present, causes the separation of saccharosate of strontium, $C_{12}H_{22}O_{11}\cdot SrO$.

The latter is removed by filtration, dissolved in water, and decomposed by carbon dioxide, which precipitates strontium carbonate. The filtered liquid is evaporated, and the sugar crystallises. The syrup which contains uncrystallisable sugar is fermented and yields alcohol on distillation. By evaporation and destructive distillation of the dry residues, potash salts remain, some methyl alcohol distils, whilst ammonia, amines and hydrocyanic acid are recovered from the gases.

FIG. 76.

Sugar Refining.—Raw sugar from the cane as well as from beet-root has a brown or yellow colour, and requires refining, which is usually carried on in separate factories. The raw sugar is dissolved in water, and the solution heated with lime and occasionally with other substances. It is then filtered and the clarified juice passed through charcoal filters. These filters consist of long cylindrical vessels filled with animal charcoal, through which the saccharine liquid percolates and is decolorised. The juice is again concentrated in vacuum-pans and crystallised. The charcoal is revivified by washing, drying, and finally heating it in closed vessels.

EXPT. 110.—Take a long wide tube open at the top and fitted at the lower end with cork and glass tap as in Fig. 76. Fill the tube with fragments of animal charcoal and allow a solution of caramel in water to trickle through. The liquid which runs out at the bottom will be colourless.

The annual production of beet sugar in Europe is about one-third of the total sugar production of the world, which is estimated at nearly 24 million tons. All European countries produce beet sugar including Great Britain, which consumes per annum $1\frac{1}{2}$ million tons (or 84 lbs. per head) of which it now produces about 140,000 tons. A certain amount of beet sugar is also produced in the United States.

Sugar Analysis.—Cane-sugar is optically active and turns the plane of polarisation to the right, $[\alpha]_D = + 66{\cdot}5°$. The most accurate method for estimating the amount of sugar present in a commercial sample is to measure the rotation by means of a polarimeter (p. 114), which, when applied for this purpose, is usually termed a *saccharimeter*. A definite weight of sugar is dissolved in water, the solution clarified with lead acetate, and introduced into a tube 20 mm. in length closed at each end by glass caps. It is then placed between the Nicol prisms of the polarimeter. The amount of deviation measured on the vernier gives directly the percentage of sugar in the sample. The deviation in the so-called half-shadow instrument is determined by an arrangement which produces an unequal illumination of the two halves of the field of view when an active solution is interposed between the Nicols. The eye-piece Nicol is then turned until equality in shade, or tint, between the two halves is restored. For an explanation of the arrangement a text-book of physics must be consulted. Another method of analysis is by determining the refractive index of the solution by means of a *refractometer*.

Properties of Cane-Sugar.—Cane-sugar crystallises from aqueous solution in monoclinic prisms which melt at 160°–161°. When allowed to deposit slowly on threads suspended in the solution, large crystals known as *sugar candy* are formed.

Cane-sugar, like glycerol, glucose, and certain other hydroxy-compounds, has antiseptic properties, and prevents the decay of putrescible matter. The sugar in candied fruits and jam acts as a preservative.

When cane-sugar is heated with a little water until it melts and the liquid begins to turn yellow, it forms, on cooling, a hard glassy mass, which is called *barley-sugar*. If sugar is heated above its melting-point, it turns brown and forms *caramel*, a semi-solid amorphous substance which is used in confectionery and for tinting spirits.

When sugar is heated in a retort, water, acetic acid, acetone, and other products distil, and a very pure form of charcoal known as *sugar charcoal* is left.

Dilute sulphuric acid hydrolyses cane-sugar and converts it into equal proportions of glucose and fructose (p. 290). The mixture

is known as *invert-sugar*, and the process as *inversion*. The name has originated from the change of sign in the rotation. Whereas cane-sugar is dextro-rotatory, when a mixture of equal quantities of the two hexoses is present, the lævo-rotation of fructose, $[\alpha]_D = -92°$, more than neutralises the dextro-rotation of glucose, $[\alpha]_D = +52·5°$, and consequently the effect is lævo-rotatory.

Strong sulphuric acid gradually decomposes and chars cane-sugar. The action is much more rapid if a little water is first added to the sugar. The charred mass then froths up and evolves carbon dioxide and sulphur dioxide.

Strong hydrochloric acid decomposes cane-sugar like the hexoses, and yields levulinic acid. Strong nitric acid oxidises cane-sugar and forms oxalic acid (p. 343).

Cane-sugar forms saccharosates or sucrosates of the metals. It combines with 1, 2, and 3 molecules of strontia. The compound with 1 molecule of strontia has already been mentioned in connection with the recovery of sugar from molasses.

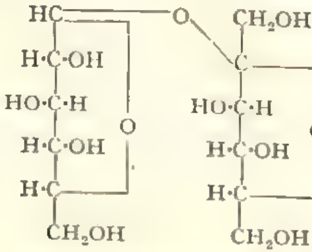
Cane-sugar is not directly fermentable by yeast. Before fermentation takes place the sugar undergoes inversion by means of the enzyme, invertase (p. 107). It has no reducing action upon an alkaline copper solution until it has been hydrolysed.

EXPT. 111.—Prepare a fresh solution of cane-sugar and divide it into two portions; boil one portion with a drop or two of dilute sulphuric acid. Add to each two drops of copper sulphate solution, and then caustic soda solution, until a clear blue solution is obtained. On boiling, cuprous oxide is precipitated by the hydrolysed sugar, but not by the unchanged cane-sugar.

It would appear from this indifference to alkaline copper solution that cane-sugar is not an aldehyde, and this view is confirmed by its behaviour with phenylhydrazine, with which it does not react.

Constitution of Cane-Sugar.—Cane-sugar has been synthesised by condensing the tetracetate of glucose with the tetracetate of γ-fructose dissolved in chloroform in presence of phosphorus pentoxide. Sucrose acetate is formed which on hydrolysis yields cane-sugar, identical with the natural product (Pictet and Vogel). The absence of the properties of aldehydes and ketones renders it probable that the union of the two hexoses is in the nature of

an anhydride or ether, formed by the linking of the aldehyde group of the one molecule to the ketone group on the other—



Cane-sugar (α-glucose-γ-fructoside).

The fact that the two hexose molecules are linked together in the way suggested results in the complete absence of any "free carbonyl" grouping. This is confirmed by the fact that pure cane-sugar gives no osazone. It may therefore be regarded either as a glucoside of fructose or as a fructoside of glucose. It has also been found that the fructose has the furanose or γ-structure in cane-sugar, but when released by hydrolysis it isomerises to the pyranose ring form.

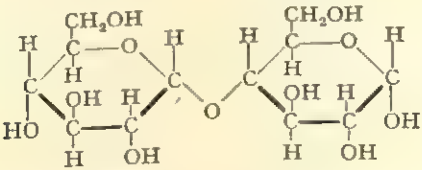
Milk-Sugar, Lactose, $C_{12}N_{22}O_{11} + H_2O$, is present in the milk of mammals. Cows' milk contains about 4·8 per cent. of lactose, together with fat, casein, albumin and a little mineral matter.

The lactose is separated by coagulating the albumin of the milk with *rennet*, or by the addition of a little acetic acid. The liquid is filtered and evaporated. The residue is milk-sugar. The whey which is obtained as a by-product in the manufacture of cheese is used as a source of milk-sugar. Milk-sugar crystallises with one molecule of water of crystallisation which it loses at 130°. It is strongly dextro-rotatory, $[\alpha]_D^{20^\circ}$ falling from + 90·0° to + 55·3°. It reduces alkaline silver and copper solutions, and forms an osazone of melting-point 200°. Milk-sugar is coloured yellow with alkalis. It is not directly fermentable with ordinary yeast, but certain bacteria readily convert it into lactic and butyric acids (p. 165). A ferment, or fungus, consisting of yellow modules known as *kephir grains*, and containing bacilli and yeast, has the property of fermenting cows' milk and converting the milk-sugar

into alcohol and carbon dioxide. *Koumiss* is a Russian beverage, and is made in a similar way by fermenting mares' milk. Milk-sugar yields *d*-glucose and *d*-galactose on hydrolysis (p. 299). Lactosazone melts at 200°.

Maltose, Malt-Sugar, $C_{12}H_{22}O_{11} + H_2O$.—Maltose is produced by the action of diastase on starch. It is the sugar which is formed in the brewing of beer or manufacture of whisky, when the malted grain is steeped in water, which is ultimately fermented and converted into alcohol (p. 108). Maltose is readily prepared in the following way: an extract of malt is made by steeping the crushed grain in water for 24 hours and adding a little of the solution, which contains diastase, to starch-paste, and heating to a temperature of 60°–65° for an hour. The paste, which has by this time become liquid, is boiled up and filtered, and evaporated on the water-bath until the liquid becomes syrupy. It is then extracted with 90 per cent. alcohol, which removes the maltose. The extract is concentrated to a syrup by evaporation, and a crystal of maltose added, which induces the crystallisation of the mass. β-Maltose crystallises from water, $[\alpha]_D^{20°}$ rising from + 118° to + 136°. A hygroscopic anhydrous α-maltose has been obtained from boiling alcohol. It reduces alkaline copper solution, and forms, with phenylhydrazine, maltosazone melting at 206°, which has a characteristic crystalline appearance under the microscope. On boiling with dilute sulphuric acid, maltose is hydrolysed, and is converted into glucose—

$$\underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose.}}{2C_6H_{12}O_6}.$$



Pyranose structure of maltose.

Maltose undergoes fermentation by yeast, the sugar being probably first hydrolysed into glucose by the action of an enzyme,

maltase, which is contained within the yeast cell. It seems, in fact, definitely proved that only the simple hexoses are directly fermentable, and that the disaccharides are all hydrolysed before conversion into alcohol and carbon dioxide can take place. The structure of maltose resembles that of lactose but consists of two glucose molecules linked together.

Raffinose, Melitriose, $C_{18}H_{32}O_{16} + 5H_2O$, is obtained from beet-root molasses, and from other sources. It is strongly dextro-rotatory, $[\alpha]_D = + 104°$. It decomposes, on hydrolysis, into glucose, fructose, and galactose.

POLYSACCHARIDES.

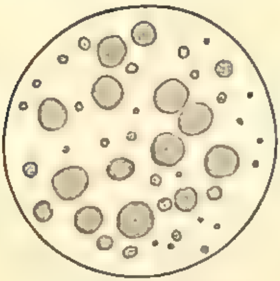
Starch, $(C_6H_{10}O_5)_n$ is found in various parts of plants, especially in the seeds and tubers, where it is stored as a reserve material to serve as nutriment for the young plant. The chief sources of starch are the potato, rice, maize, and wheat, which contain the following average percentages of starch :—

Potato	15–20 per cent.
Wheat, and other cereals	60–65 ,,
Maize	65 ,,
Rice	75–80 ,,

Arrow-root starch is obtained from the tubers of certain species of maranta, a plant which grows in the tropics; *sago* is derived from the pith of the sago-palm; amd *tapioca* is prepared from the tubers of manihot or cassava. In the case of *sago*, the starch is moistened and pressed through a sieve, the grains being rounded and hardened by being rubbed together and heated on hot metal plates. Sometimes potato starch is given the form of sago or tapioca.

Manufacture of Starch.—In England, starch is prepared chiefly from rice, whilst potatoes are employed in Germany, and maize, or Indian corn, in the United States. The process of manufacture is mainly a mechanical one. The material is softened and crushed, and then washed by a stream of water through revolving cylinders

covered with fine wire or silk, which act as sieves, allowing the starch granules to pass, but retaining the gluten, or vegetable protein and cellulose, or cell-wall. The starch is further washed on sloping troughs to remove the lighter fibrous particles, and is then drained in a centrifugal extractor and dried. Rice, maize, and wheat, in which the starch is firmly cemented to the gluten of the grain, is disintegrated before washing, either by fermentation or by the action of dilute caustic soda, which dissolves the protein.



Wheat starch (highly magnified).

Potato starch (highly magnified).

FIG. 77.

EXPT. 112.—Enclose a handful of flour in a small muslin bag and knead it under water. The starch grains pass through the meshes of the muslin into the water and produce a milky liquid, whilst the gluten remains in the bag as a tough, sticky mass. Examine some of the milky fluid under a good microscope, and notice the appearance of the grains.

Properties of Starch.—The appearance of different kinds of starch under the microscope is characteristic. The grains may be round, elliptical, or angular, and of different sizes. In Fig. 77 is shown the microscopic appearance of wheat and potato starch of the same magnification.

The grains consist of concentric rings, or layers, arranged round a nucleus. Between crossed Nicols they present the appearance of a doubly refracting crystal. Starch is insoluble in cold water, but, when heated, the granules swell up and burst, forming a

slightly opalescent solution, which on cooling sets to a stiff paste known as *starch-paste*. The soluble portion is termed *granulose*, and the insoluble part which renders the liquid turbid is known as *starch cellulose*. When starch is heated with water under pressure, with glycerol, or with dilute acids, it dissolves in hot water, and separates on cooling as an amorphous white powder, known as *soluble starch*. When starch is heated below a point at which it becomes discoloured, it is converted into *dextrin* (see below). The most characteristic reaction for starch is its behaviour with iodine. A solution of starch-paste in water is coloured blue by free iodine. The colour disappears on warming, but returns when the liquid cools. The reaction is very delicate, 0·003 milligram of iodine being detected in this way. When extract of malt in water which contains the enzyme diastase is added to starch paste, and the mixture maintained at a temperature of about 60°, the starch soon liquefies and becomes limpid. If iodine solution is added at intervals to portions of the solution, from the moment liquefaction occurs the following appearances will be observed :—A blue solution is first obtained. This is the ordinary reaction for starch or soluble starch. The coloration of succeeding portions is purple, then red, until, finally, no coloration is produced. These changes are caused by the disintegration of the starch molecule into simpler compounds known as *dextrins*, the latter being ultimately decomposed and converted into maltose (p. 307), when the action ceases. Saliva and pancreatic juice, which contain hydrolytic enzymes (ptyalin) resembling diastase, produce a similar effect on starch. An analogous series of changes is brought about by boiling starch with dilute sulphuric acid, but as the maltose is also hydrolysed, the starch is almost completely converted into glucose (p. 290).

It has recently been shown that phosphates play an important part in the synthesis of starch by plants.

Expt. 113.—Make a thin solution of starch paste by grinding up about 2 grams with a little cold water and pouring the mixture into 50 c.c. of boiling water. Divide the solution into three parts. Add a few c.c. of malt extract to one portion, and warm to 60°; add a little saliva to another; and boil a third portion with a few drops of dilute

sulphuric acid. Test a portion of each both with iodine solution and alkaline copper solution from time to time. In each case the blue colour will gradually give place to violet, then red, and finally disappear, whilst the presence of maltose on glucose will be indicated by the precipitation of cuprous oxide.

Attempts to determine the molecular weight by the cryoscopic method are untrustworthy, as the experimental error is probably very great, and other physical methods, based on determinations of viscosity or sedimentation by means of the ultra-centrifuge, are equally misleading. A more promising line of investigation, which is due to Haworth, is based on chemical rather than on physical evidence. It depends on analysis of the breakdown products of starch, which has been previously methylated. The view is taken that chains consisting of about 30 glucose molecules are linked together in much the same way as in maltose, and that one end of each chain is linked across to an intermediate carbon atom in the next chain.

Uses of Starch.—Starch is used for sizing and stiffening paper and cloth, for laundry purposes and for the manufacture of dextrin or British gum.

Dextrin, $(C_6H_{10}O_5)_n$, is the name given to a mixture of products obtained from starch by the action of heat or by partial hydrolysis with diastase or dilute acids. These substances are intermediate in composition between starch and maltose, and, like them, can be hydrolysed to glucose. Dextrin is usually manufactured by moistening starch with a mixture of dilute nitric acid and hydrochloric acid and heating to 100°–125° C. When no acid is used, a higher temperature is required (about 250° C.). Dextrin is a yellowish, amorphous powder with a peculiar smell. It dissolves in water to form a clear mucilage, and is employed under the name of *British gum.*

Cellulose, $(C_6H_{10}O_5)_n$, is a fundamental constituent of the cell-walls of plants, and forms the framework, or skeleton, of vegetable tissues. It is probably elaborated from simpler carbohydrates secreted by the protoplasm of the cell. Cellulose in a pure state is best known to us as cotton-wool, linen, and paper. The difference between cotton and linen is due rather to the structure of the fibres than to their chemical composition. Both kinds of fibre contain a small quantity of mineral matter, which is left as ash on

burning the organic matter. The mineral matter is almost entirely removed by the action of hydrofluoric acid. The best filter papers are prepared by treatment with this acid, after which they are well washed with water, alcohol, and ether. These papers, which are sometimes known as Swedish filter papers, consist of cellulose in its purest form. A careful study of the cellular tissues has shown that cellulose does not represent one only, but several substances, which may be differentiated by the products which they yield on hydrolysis. Some, like cotton and linen, give glucose; others mannose; and others, again, galactose and the pentoses, xylose and arabinose (see p. 315). Cotton may be distinguished from wool by the fact that the latter contains sulphur. If caustic soda is added to a little lead acetate solution until the precipitate of hydrated oxide redissolves, woollen fibre or cloth immersed in the liquid and warmed will give a precipitate of lead sulphide. Cotton, moreover, is readily inflammable, whereas wool and silk shrivel, blacken and emit a smell of burnt hair.

Properties of Cellulose.—Cellulose is an unusually inert substance. It is scarcely affected by chlorine, or by dilute acids or alkalis. These reagents are consequently employed in separating the fibre from encrusting matter, resin, gum, and wax, with which it is usually associated. In the manufacture of paper and in the cleaning and bleaching of cotton, both caustic soda and hypochlorites are used. It is this inertness towards the common reagents which renders paper so serviceable as a filtering medium. With oxidising agents cellulose is converted into *oxycellulose*.

A strong solution of caustic alkalis produces a curious thickening and gelatinising of the walls of the fibre, which causes the cellulose to shrink and become translucent. The effect of pouring a strong solution of caustic soda on to filter paper is very marked. It rapidly thickens and contracts. When applied to cotton fibre and cloth the process is known, after its discoverer, John Mercer, as *mercerising*, and is used for producing crinkled surfaces on cotton fabrics. Strong sulphuric acid rapidly attacks and dissolves cellulose. This reagent is used for "carbonising," *i.e.* removing the cotton from mixed fabrics, animal fibres (wool and silk) being unaffected. If the sulphuric acid is diluted with water

in the proportion of 2 volumes of sulphuric acid to 1 volume of water, and a piece of filter paper dipped into the liquid, the paper becomes immediately tough and translucent. When freed from acid and dried, it is known as *parchment paper*. Fuming hydrochloric acid or boiling dilute sulphuric acid breaks up the cellulose molecule and yields glucose. The decomposition is hastened by dissolving cellulose in strong sulphuric acid, then diluting with water and boiling. Zinc chloride in hydrochloric acid dissolves cellulose, and so also does a solution of cupric oxide in ammonia, known as *Schweitzer's reagent*. The latter solution is prepared by precipitating copper sulphate with caustic soda in the cold, washing the precipitate, and dissolving it whilst still moist in a little strong ammonia solution. Cotton-wool rapidly gelatinises in the solution and ultimately dissolves. The cellulose is thrown down from the solution by the addition of acids, alcohol, or even common salt, in the form of a gelatinous precipitate resembling alumina. This reaction is used for producing an artificial silk (see below) and also for preparing *Willesden paper*. The surface of the paper is moistened with the ammoniacal cupric oxide, which gelatinises the surface fibres, and, after drying, renders the paper impervious to water. Cellulose is readily acted upon by strong nitric acid, or a mixture of nitric and sulphuric acid, and yields a series of cellulose nitrates, *pyroxylins* or *nitro-celluloses*. These substances are not nitro-compounds, seeing that they are hydrolysed by alkalis and the nitrogen removed as nitrate of the alkali. They must be regarded as nitric esters of cellulose. The most important of these compounds is gun-cotton.

Gun-cotton, *Cellulose hexanitrate*, $[C_{12}H_{14}O_4(O{\cdot}NO_2)_6]_n$.—Gun-cotton is prepared by steeping pure cotton-wool in a mixture of 3 parts of fuming nitric acid and 1 part of strong sulphuric acid for twenty-four hours at a temperature not exceeding 10°. It is then removed and carefully washed with water until free from acid. When dry, the cotton, though still preserving its fibrous texture, is much more inflammable and burns with remarkable rapidity. When compressed into cartridges and detonated, it forms a powerful explosive. Gun-cotton is insoluble in a mixture of alcohol and ether, but dissolves in acetone, forming a jelly. This solution is mixed with nitro-glycerine in the preparation of cordite (p. 284).

When gun-cotton is dissolved in nitro-glycerine, it forms blasting gelatine (p. 284). The lower nitrates of cellulose (tetra- and penta-nitrates) are prepared by a modification of the above reaction and are used for various purposes.

Collodion is the solution of the lower nitrates in a mixture of alcohol and ether. On evaporation of the solvent a transparent film of considerable tenacity remains. It is used for producing *artificial silk* (Chardonnet's process). The solution, to which dilute sulphuric acid is added, is forced through a fine orifice into water, where it is at once coagulated and forms a fine transparent thread of considerable toughness. The threads when wound on a reel, and twisted, produce a silky fibre, which is rendered non-explosive by denitration with ammonium sulphide.

Artificial silk is also prepared from the gelatinous mass obtained by dissolving cotton in Schweitzer's reagent (Pauly), and also from the viscous product (viscose) made by treating cellulose or wood pulp with a mixture of carbon bisulphide and caustic alkali (Cross and Bevan). Cellulose acetate is used for the same purpose and is known as *acetate silk* or "*Celanese*". In all cases the viscid, transparent liquid is squeezed through a fine aperture and subsequently rendered insoluble. The same materials when pressed through thin slits produce cinematograph and photographic films. Unlike the nitrates, cellulose acetate is not readily inflammable.

Celluloid, *Xylonite*, consists of the lower nitrates of cellulose. They are dissolved with camphor in acetone, alcohol or amyl acetate, and other substances added. The mixture forms a plastic mass, which can be worked up for a variety of purposes such as knife-handles, piano-keys, combs and for imitation ivory, amber and tortoiseshell. It is, naturally, extremely inflammable though non-explosive.

Manufacture of Paper.—A great variety of materials are employed in the manufacture of paper, such as linen and cotton rags, esparto grass, straw, and wood. The material is first disintegrated by mechanical means. The fabrics are torn up and the straw and wood cut into small pieces. The materials are converted into pulp by boiling with caustic soda in closed boilers heated by steam under pressure. Wood-pulp is prepared by using a strong solution of calcium bisulphite in place of caustic alkalis. The pulp is run

out, washed and bleached with bleaching liquor, and again washed. It is then ready to be made into paper.

Inulin, $(C_6H_{10}O_5)_n + H_2O$, is found in dahlia tubers and in the tubers, bulbs, and roots of other plants, where it appears to take the place of starch. It is a white powder, which does not give a blue colour with iodine. On hydrolysis it yields fructose (p. 296).

Glycogen, $(C_6H_{10}O_5)_n$, is widely distributed in the animal kingdom, and is sometimes known as *animal starch*. It appears to play the part of a reserve material, for it quickly disappears when food is not taken. Glycogen is found in the liver and in small quantities in muscle. It is also found in certain fungi, and is very plentiful in molluscs. Oysters contain as much as 9 per cent. of glycogen. It is a white amorphous powder, which dissolves in hot water, and is precipitated by alcohol. Iodine colours it brown. It is strongly dextro-rotatory. Submitted to the action of diastase, it yields dextrin, maltose, and glucose.

Gums are transparent, glassy, amorphous substances, which are exuded from plants and are known as *pentosans*. They form a mucilage with water, from which the gum is precipitated by alcohol. They do not reduce Fehling's solution, but are hydrolysed by acids into monosaccharides. The monosaccharides are pentoses, the pentosans bearing the same relation to the pentoses as starch to glucose. The two pentoses, *arabinose* and *xylose*, are obtained from certain gums. *Gum arabic* is an exudation from the bark of several species of acacia. It consists of the calcium and potassium salts of arabic acid. When hydrolysed with dilute sulphuric acid, it yields *arabinose*, $C_5H_{10}O_5$. *Wood gum* is widely distributed throughout the vegetable kingdom. It is extracted from the wood of various trees by digestion with caustic alkalis and precipitation by alcohol. It is a white powder, which, on hydrolysis, yields *xylose*, $C_5H_{10}O_5$. d-*Ribose* has been shown to be a constituent of the nucleic acid of cell nuclei.

EXPT. 114.—The presence of pentoses may be shown by their behaviour with a solution of phloroglucinol (p. 469) or orcinol in strong hydrochloric acid. A pine shaving, or gum arabic, on gently warming with the solution, turns a bright cherry-red with the former and violet with the latter reagent, showing the presence of a pentose in both cases.

QUESTIONS ON CHAPTER XX

1. Describe the system of classification adopted in the case of the carbohydrates. How could you readily distinguish a carbohydrate from a polyhydric alcohol?

2. What are the chief reactions of the monosaccharides? Which of the disaccharides give similar reactions?

3. Describe the preparation of glucose and fructose from cane-sugar. How can the two sugars be distinguished? How is fructose obtained from glucose? Why are the names glucose and fructose used in preference to the older names of dextrose and lævulose?

4. Give the products of hydrolysis of the three principal disaccharides. How is maltose prepared? How is it distinguished from glucose?

5. How are the following compounds inter-related: starch, dextrin, glucose, mannitol, gluconic acid, and saccharic acid?

6. What is the experimental evidence for the conclusion that glucose contains an aldehyde group and fructose a ketone group? How does phenylhydrazine react with each of these sugars?

7. How can the hydrolysis of starch, cellulose, cane-sugar, inulin, and glycogen be effected? State the properties of their hydrolytic products.

8. To what class of bodies does glucose belong? Where does it occur? From what sources is it made, and how can it be recognised?

9. By what properties and reactions would you distinguish a solution of cane-sugar from a solution of glucose?

10. How would you demonstrate the production of glucose from cane-sugar and starch respectively?

11. What effect is produced on starch by the action of (1) heat, (2) dilute sulphuric acid, (3) nitric acid?

12. What are the principal differences between starch and cellulose? What evidence exists as to the molecular weights of these substances?

13. What is the action of (1) nitric acid, (2) sulphuric acid, and (3) caustic soda on cellulose?

14. How are the following prepared: *starch*, *British gum*, *gun-cotton*, *Willesden paper*, *celluloid*, *collodion*, and *cordite*?

15. Describe and explain the changes which starch undergoes when acted on by malt extract. How could these changes be demonstrated?

CHAPTER XXI

DERIVATIVES OF THE FATTY ACIDS

1. The Hydroxy-Acids

The Hydroxy-Acids or *oxy-acids* are compounds which combine the properties of alcohols and acids. They contain, in other words, both hydroxyl and carboxyl groups. They include some of the most important acids derived from the vegetable and animal kingdoms. According to the number of hydroxyl groups present in the compound, the acid is known as a mono-, di-, tri-, etc., hydroxy-acid. Glycollic acid (see below) is a monohydroxy-acid; glyceric acid (p. 281) is a dihydroxy-acid; gluconic acid (p. 291) is a pentahydroxy-acid.

We shall begin with the study of the monohydroxy-monobasic acids, that is to say, compounds which contain one hydroxyl and one carboxyl group. They may be regarded as hydroxy-derivatives of the fatty acids.

Formation of the Hydroxy-Acids.—They are obtained by the careful oxidation of the glycols, whereby one carbinol group is converted into a carboxyl group. The method is, however, seldom used on account of the difficulty of preparing the glycols. Ethylene glycol is converted by the action of dilute nitric acid into hydroxy-acetic or glycollic acid—

$$\underset{\text{Glycol.}}{\begin{array}{l} CH_2(OH) \\ | \\ CH_2(OH) \end{array}} + O_2 = \underset{\text{Glycollic acid.}}{\begin{array}{l} CH_2(OH) \\ | \\ CO{\cdot}OH \end{array}} + H_2O.$$

A more common method is to boil with water salts of mono-halogen derivatives of the fatty acids. The chlorine is thereby replaced by hydroxyl. Potassium monochloracetate yields glycollic acid (p. 323)—

$$\underset{\text{Potassium monochloracetate.}}{\begin{array}{l} CH_2\boxed{Cl + H}OH \\ | \\ CO{\cdot}OK \end{array}} = \underset{\text{Glycollic acid.}}{\begin{array}{l} CH_2(OH) \\ | \\ CO{\cdot}OH \end{array}} + KCl.$$

A third method is to hydrolyse the cyanhydrins of the aldehydes and ketones. In this manner the cyanogen group is converted into a carboxyl group. Acetaldehyde cyanhydrin forms hydroxy-propionic acid; acetone cyanhydrin yields hydroxyisobutyric acid—

$$\begin{array}{l} CH_3 \\ | \\ CH{<}\begin{array}{l}OH\\ CN\end{array} \end{array} + 2H_2O = \begin{array}{l} CH_3 \\ | \\ CH{<}\begin{array}{l}OH\\ CO{\cdot}OH\end{array} \end{array} + NH_3.$$

Hydroxy-propionic acid.

$$\begin{array}{l} CH_3 \\ | \\ C{<}\begin{array}{l}OH\\ CN\end{array} \\ | \\ CH_3 \end{array} + 2H_2O = \begin{array}{l} CH_3 \\ | \\ C{<}\begin{array}{l}OH\\ CO{\cdot}OH\end{array} \\ | \\ CH_3 \end{array} + NH_3.$$

Hydroxyisobutyric acid.

It should be noted that by this method the hydroxyl and carboxyl groups are necessarily linked to the same carbon atom.

Properties of the Hydroxy-acids.—The hydroxy-acids are more soluble in water than the corresponding fatty acids. This may be ascribed to the additional hydroxyl group. For the same reason they are less volatile, just as the glycols are less volatile than the monohydric alcohols. Whereas acetic acid melts at 16°, glycollic acid melts at 80°, and cannot be distilled unchanged. The hydroxy-acids form salts with the bases in which the hydrogen of the carboxyl group is replaced by a metal, whereas metallic sodium replaces hydrogen of the hydroxyl as well as of the carboxyl group. Phosphorus pentachloride likewise replaces both hydroxyl groups by chlorine. The action of sodium and phosphorus pentachloride on glycollic acid produces the following compounds—

$$\begin{array}{l} CH_2(ONa) \\ | \\ CO{\cdot}ONa \end{array}$$

Disodium glycollate.

$$\begin{array}{l} CH_2Cl \\ | \\ CO{\cdot}Cl. \end{array}$$

Chloracetyl chloride.

Chloracetyl chloride is both an alkyl chloride and an acyl chloride. Water rapidly attacks the acyl chloride group and monochloracetic acid is formed—

$$\begin{array}{l} CH_2{\cdot}Cl \\ | \\ CO{\cdot}\boxed{Cl + H}OH \end{array} = \begin{array}{l} CH_2Cl \\ | \\ CO{\cdot}OH \end{array} + HCl.$$

On continued boiling the alkyl chlorine atom is also replaced by hydroxyl as already explained.

The two hydrogen atoms of the hydroxyl and carboxyl groups may be replaced separately or together by alkyl groups.

In the latter case a compound is formed which is both ether and ester. Ethyl glycollic ester has the following formula—

$$\begin{array}{l} CH_2{\cdot}OC_2H_5 \\ | \\ CO{\cdot}OC_2H_5. \end{array}$$

Ethylglycollic ester.

Hydrobromic acid attacks the alcohol hydroxyl and replaces it by bromine; hydriodic acid acts on the same group as a reducing agent and replaces it by hydrogen. Glycollic acid yields in the one case monobromacetic acid and in the other acetic acid—

$$\begin{array}{l} CH_2\boxed{OH + H}Br \\ | \\ CO{\cdot}OH \end{array} = \begin{array}{l} CH_2Br \\ | \\ CO{\cdot}OH \end{array} + H_2O.$$

Monobromacetic acid.

$$\begin{array}{l} CH_2\boxed{I + I}H \\ | \\ CO{\cdot}OH \end{array} = \begin{array}{l} CH_3 \\ | \\ CO{\cdot}OH \end{array} + I_2.$$

Acetic acid.

On oxidation, the alcohol group is converted into an aldehyde or a ketone group, according to whether it is a primary or secondary alcohol group. Glycollic acid may be transformed into glyoxalic and finally into oxalic acid by regulated oxidation. Hydroxy-propionic acid or lactic acid forms a ketonic acid, pyruvic acid, and then acetic acid—

$$\underset{\text{Glycollic acid.}}{\begin{array}{l} CH_2OH \\ | \\ CO{\cdot}OH \end{array}} \longrightarrow \underset{\text{Glyoxalic acid.}}{\begin{array}{l} CHO \\ | \\ CO{\cdot}OH \end{array}} \longrightarrow \underset{\text{Oxalic acid.}}{\begin{array}{l} CO{\cdot}OH \\ | \\ CO{\cdot}OH \end{array}}$$

$$\underset{\text{Lactic acid.}}{\begin{array}{l} CH_3 \\ | \\ CH(OH) \\ | \\ CO{\cdot}OH \end{array}} \longrightarrow \underset{\text{Pyruvic acid.}}{\begin{array}{l} CH_3 \\ | \\ CO \\ \vdots \\ CO{\cdot}OH \end{array}} \longrightarrow \underset{\text{Acetic acid and Carbon dioxide.}}{\begin{array}{l} CH_3 \\ | \\ CO{\cdot}OH \\ + \\ CO_2 \end{array}}$$

Isomerism of the Hydroxy-acids.—Among the hydroxy-acids containing more than 2 carbon atoms it is clear that the hydroxyl

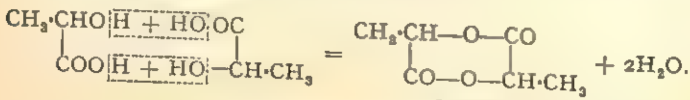
group may be attached to different carbon atoms of the chain. Hydroxypropionic acid or lactic acid exists in two isomeric forms—

$CH_3 \cdot CH(OH) \cdot CO \cdot OH$ — α-Hydroxypropionic acid.

$CH_2(OH) \cdot CH_2 \cdot CO \cdot OH$ — β-Hydroxypropionic acid.

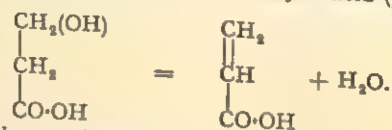
They are distinguished like the halogen derivatives of the fatty acids (p. 153) by lettering the carbon atoms α, β, γ, etc., beginning with the carbon atom next to the carboxyl group.

Properties of the α-, β-, γ-, and δ-Hydroxy-acids.—The position of the hydroxyl group determines the character of the products obtained on heating the different hydroxy-acids. When the α-hydroxy-acids are heated, two molecules react with the elimination of two molecules of water. Hydroxypropionic acid gives lactide—



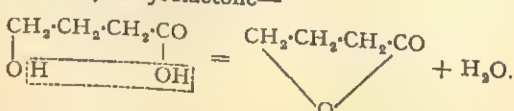
Lactide.

The β-hydroxy-acids lose a molecule of water and form unsaturated acids. β-Hydroxypropionic acid forms acrylic acid (p. 270)—



β-Hydroxypropionic acid. Acrylic acid.

The γ- and δ-hydroxy-acids also lose a molecule of water and form what are known as inner esters or *lactones*. The product may be regarded as an ester derived from the action of an alcohol on an acid; but the alcohol and acid are part of the same molecule. γ-Hydroxybutyric acid forms γ-butyrolactone—



γ-Hydroxybutyric acid. γ-Butyrolactone.

That the γ- and δ-hydroxy-acids, unlike the α- and β-hydroxy-compounds, form lactones has been explained by the space arrangement of the carbon linkages (p. 88). If a number of carbon atoms are linked together the chain which they form will not be straight as usually represented, but coiled; and as the linkages diverge at an angle of about 109°, the tendency will be to form a closed chain when the number of carbon atoms exceeds 4. This is shown in the diagram (Fig. 78).

In other words, the groups attached to the end carbon linkages of a chain of 4 or 5 carbon atoms are brought within closer range than when fewer carbon atoms are present in the compound. Thus, mutual action can occur, and new combinations are formed between the end groups of the chain.

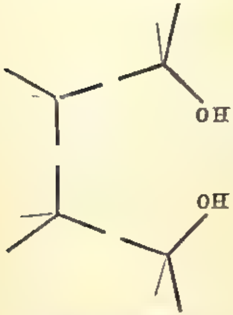


FIG. 78.—Space arrangement of four Carbon groups.

Carbonic acid, (OH)CO·OH, which, though unknown in the free state, forms salts and esters, might be regarded as the first representative of the monohydroxy-acids; but it is distinctly a dibasic acid, for it contains 2 hydrogen atoms replaceable by metals in the salts and by alkyl groups in the esters. It must, therefore, be classed with the dibasic or dicarboxylic acids (p. 333).

Glycollic Acid, *Hydroxyacetic acid*, $CH_2(OH)\cdot COOH$, is the first member of the series. It is found in unripe grapes, and in the leaves of the Virginian creeper. It is most readily obtained by boiling potassium chloracetate with water. The liquid is evaporated and the glycollic acid extracted with acetone, in which it readily dissolves, leaving the potassium chloride undissolved—

$$CH_2Cl\cdot CO\cdot OK + H_2O = \underset{\text{Glycollic acid.}}{CH_2(OH)\cdot COOH} + KCl.$$

It is a colourless, crystalline substance, which melts at 80°.

Glyoxal, CHO·CHO, is the dialdehyde of glycol, and may be regarded as an intermediate product between glycol and glyoxalic acid, CHO·CO·OH (p. 326). It is prepared by oxidising acetaldehyde with nitric acid. Equal parts of aldehyde and water are mixed together and poured into a cylinder. A layer of water is formed below the aldehyde solution by pouring the water carefully down a thistle funnel. Below this a layer of strong nitric acid is poured, and the three layers are allowed to diffuse slowly. A polymer of glyoxal is formed and may be separated by evaporation, as a colourless amorphous mass. Glyoxal itself may be obtained from the polymeric form by distilling with phosphorus pentoxide or acetic anhydride, and forms yellow crystals, m.p. 15°. It exhibits the properties of an aldehyde, but in a twofold degree, reacting with two molecules of hydroxylamine and phenylhydrazine, forming a bisulphite compound with two molecules of sodium bisulphite and a diphenylhydrazone; it also combines with two molecules of hydrocyanic acid to give a dicyanhydrin (p. 131).

Lactic Acid, *Ethylidene lactic acid, α-Hydroxypropionic acid,* CH_3·CH(OH)·CO·OH.—The α-hydroxy-acid or ordinary lactic acid is present in sour milk, from which it was first isolated by Scheele in 1780. It is produced in milk by the lactic fermentation of milk-sugar (p. 306). Lactic acid is more readily prepared from cane-sugar or starch, the operation being similar to that used in the preparation of butyric acid (p. 165). Cane-sugar is dissolved in water, and fermentation is caused by inoculation with a pure culture of *Bacillus aceti lacti* from sour milk. Nitrogen must be present either as protein or as a salt, and zinc or calcium carbonate must be added to neutralise the free lactic acid. The ferment is added in the form of decayed cheese and sour milk, and the mixture is kept at a temperature of 40°–50° for several days. Crystalline crusts of zinc or calcium lactate separate, and are removed and recrystallised. The acid is obtained by decomposing the salts with sulphuric acid and extracting with ether. On evaporating the ether, the lactic acid remains as a colourless viscid liquid which possesses a sour smell and taste. It is also obtained from α-chloro- or bromo-propionic acid by boiling with water (p. 153), and by the hydrolysis of acetaldehyde cyanhydrin (p. 131). When pure, it melts at 18° and distils at 1 mm. pressure unchanged. At the ordinary pressure it is converted into lactide (p. 320). Boiled with dilute sulphuric acid, it decomposes into acetaldehyde and formic acid—

$$CH_3\cdot CH(OH)\cdot CO\cdot OH = CH_3\cdot CHO + H\cdot COOH.$$

The calcium and zinc salts of lactic acid readily crystallise from hot water, and are characteristic of the acid. The calcium salt has the composition $(CH_3\cdot CH(OH)\cdot COO)_2Ca + 5H_2O$; the zinc salt has the formula $(CH_3\cdot CH(OH)\cdot COO)_2Zn + 3H_2O$.

Para- or Sarcolactic Acid, CH_3·CH(OH)·CO·OH.—The acid is found in muscle, to which it imparts an acid reaction, and is consequently present in the juice of flesh. It is found to accompany muscular activity and is apparently formed from glycogen (p. 315). A convenient source of the acid is Liebig's extract of meat. The extract is dissolved in water, and the albumin precipitated by alcohol. The alcohol is then driven off, the liquid acidified, and the sarcolactic acid extracted with ether. It is optically active, turning the plane of polarisation to the right, and in this respect it differs from the sour milk acid, which is inactive. Moreover, the zinc salt

of sarcolactic acid contains only two molecules of water of crystallisation. In all other chemical properties the two acids appear to be identical. Sarcolactic acid can also be obtained from ordinary lactic acid by the action of *Penicillium glaucum*, which destroys the lævo-rotatory form.

The optical activity of the acid is due to the presence of an asymmetric carbon atom (p. 115). This is readily explained by the following formula (the asymmetric carbon atom is in thick type)—

$$\begin{array}{c} CH_3 \\ | \\ H\text{—}\mathbf{C}\text{—}OH \\ | \\ CO\cdot OH \end{array}$$

Sarcolactic acid.

But this formula is also that of the sour milk acid which owes its optical inactivity to the fact that it is the racemic form, *i.e.*, a mixture of both optical isomerides (Chap. XXIII).

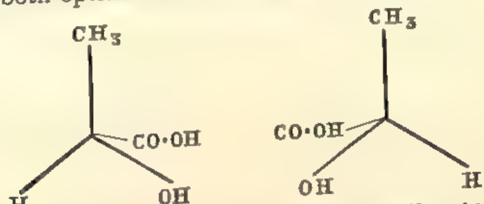


FIG. 79.—Stereo-isomeric forms of Lactic acid

Hydracrylic Acid, *Ethylene lactic acid*, *β-Hydroxypropionic acid*, $CH_2(OH)\cdot CH_2\cdot CO\cdot OH$.—This represents a third lactic acid, which, however, has a different structure from either of the previous acids. It is named hydracrylic acid from the fact of its losing a molecule of water on heating, a property of all β-hydroxy-acids (p. 320), and forming acrylic acid. It is termed also ethylene lactic acid to denote that the acid contains the radical ethylene $CH'_2\cdot CH'_2$, thereby distinguishing it from ordinary lactic acid or ethylidene lactic acid, which contains the ethylidene radical $CH_3\cdot CH''$. The designation β-hydroxypropionic acid has already been explained (p. 320). Hydracrylic acid has been obtained synthetically by boiling the β-chloro- and bromo-propionic acids with water, or by acting upon ethylene chlorhydrin (p. 249) with potassium cyanide. The cyanhydrin, thus formed, yields the acid on hydrolysis. These changes are represented as follows :—

$$\underset{\text{Ethylene chlorhydrin.}}{\begin{array}{l} CH_2(OH) \\ | \\ CH_2Cl \end{array}} \xrightarrow{KCN} \underset{\text{Ethylene cyanhydrin.}}{\begin{array}{l} CH_2(OH) \\ | \\ CH_2\cdot CN \end{array}} \xrightarrow{H_2O} \underset{\text{Ethylene lactic acid.}}{\begin{array}{l} CH_2(OH) \\ | \\ CH_2\cdot CO\cdot OH. \end{array}}$$

Hydracrylic acid is a thick, syrupy liquid resembling ordinary lactic acid.

2. The Amino-Acids

The Amino-Acids derive their interest from their occurrence among the decomposition products of albuminoid substances and proteins (p. 596). The amino-derivatives of the fatty acids are fatty acids in which one atom of hydrogen of the alkyl group is replaced by the amino (NH_2) group. They are consequently both amines and acids, the result being that they are neutral substances.

Glycine, *Glycocoll, Amino-acetic acid,* $CH_2(NH_2)\cdot CO\cdot OH$.—This compound was originally prepared by boiling gelatine or glue with dilute sulphuric or hydrochloric acid or caustic soda. It crystallises in large four-sided prisms which have a sweet taste. Hence, it received the name of glycocoll (γλυκύς, sweet; κόλλα, glue) or gelatine-sugar. It is most conveniently prepared by mixing chloracetic acid and ammonia solution—

$$\underset{\text{Chloracetic acid.}}{\begin{array}{l} CH_2Cl \\ | \\ CO\cdot OH \end{array}} + 3NH_3 = \underset{\text{Glycine ammonia.}}{\begin{array}{l} CH_2(NH_2) \\ | \\ CO\cdot ONH_4 \end{array}} + NH_4Cl.$$

After standing, the solution is concentrated and the glycine converted into the crystalline copper salt by boiling with copper carbonate.

The copper salt, $(C_2H_4NO_2)_2Cu + H_2O$, is then separated, dissolved in water, and decomposed by hydrogen sulphide. The sulphide of copper is removed by filtration, and the solution concentrated until the glycine begins to crystallise. The copper salt of glycine as well as of certain other amino fatty acids has a deep blue colour.

Expt. 115.—Dissolve a crystal of glycine in water and add a single drop of copper sulphate solution. A blue colour is at once produced, which is of a different shade from that of copper sulphate and is much more intense. Ferric chloride gives a deep red colour with glycine.

Glycine exhibits the property of a primary amine in its behaviour

with nitrous acid (p. 202). The amino group is replaced by hydroxyl, nitrogen is evolved, and glycollic acid is formed—

$$\begin{array}{l} CH_2NH_2 \\ | \\ COOH \end{array} + HNO_2 = \begin{array}{l} CH_2(OH) \\ | \\ COOH \end{array} + N_2 + H_2O.$$

It differs from an amide inasmuch as it does not evolve ammonia when heated with a solution of caustic soda.

Derivatives of Glycine.—**Hippuric Acid**, or benzoyl glycine, is glycine in which a hydrogen atom of the amino group is replaced by the aromatic acid radical *benzoyl* (p. 486). The formula of hippuric acid is—

$$\begin{array}{l} CH_2{\cdot}NH(CO{\cdot}C_6H_5) \\ | \\ CO{\cdot}OH \end{array}$$

Hippuric acid, or
Benzoyl glycine.

It is found in the urine of herbivorous animals, and crystallises in long white prisms, which readily decompose on boiling with strong hydrochloric acid into benzoic acid and glycine—

$$\begin{array}{l} CH_2{\cdot}NH \\ | \\ CO{\cdot}OH \quad H \end{array} \begin{array}{c} CO{\cdot}C_6H_5 \\ + \\ OH \end{array} = \begin{array}{l} CH_2{\cdot}NH_2 \\ | \\ CO{\cdot}OH \end{array} + \underset{\text{Benzoic acid.}}{C_6H_5CO{\cdot}OH.}$$

Expt. 116.—Boil a few crystals of hippuric acid with strong hydrochloric acid. Cool and filter off the crystals of benzoic acid, add a slight excess of ammonia to the filtrate, and boil until the solution is neutral and the excess of ammonia driven off. The addition of a few drops of copper sulphate solution will produce the characteristic deep blue colour of copper glycine.

Sarcosine, *Methyl glycine*, $(CH_3NH)CH_2{\cdot}COOH$, is obtained by boiling creatine (see below) with baryta solution. It may be prepared synthetically by the action of methylamine on chloracetic acid—

$$\begin{array}{l} CH_2\boxed{Cl + H}NHCH_3 \\ | \\ COOH \end{array} = \begin{array}{l} CH_2{\cdot}NHCH_3 \\ | \\ COOH \end{array} + HCl.$$

Betaine, *Trimethyl glycine*, $HO(CH_3)_3N{\cdot}CH_2{\cdot}COOH$, is present in beet-root molasses (p. 301), and is the probable source of trimethylamine, which the dry beet residues yield on distillation (p. 207). It is closely related to choline, from which it may be obtained by oxidation (p. 208*a*). Its synthesis from chloracetic acid and trimethylamine establishes its constitution—

$$\underset{\text{Betaine.}}{\begin{array}{l} N(CH_3)_3OH \\ | \\ CH_2{\cdot}COOH \end{array}} \qquad \underset{\text{Betaine anhydride}}{\begin{array}{lcl} N(CH_3)_3 & & O \\ | & & | \\ CH_2 & \text{———} & CO \end{array}}$$

When heated to 100° it loses a molecule of water and forms the anhydride.

Creatine, *Methylguanidine acetic acid*, $C_4H_9N_3O_2$, is present in small quantity in the juice of meat together with sarcolactic acid. It is readily obtained by precipitating the albumin from meat extract with basic lead acetate. The liquid is filtered and the lead removed with hydrogen sulphide. On concentrating the filtrate on the water-bath, a brown, viscid liquid remains, from which, on cooling, creatine crystallises in long prisms. When boiled with baryta water creatine is hydrolysed, and yields urea and sarcosine—

$$\begin{array}{l} \quad NH_2 \\ \quad | \\ HN{:}C\text{—}N(CH_3){\cdot}CH_2{\cdot}COOH \\ \qquad\qquad \text{Creatine.} \\ + \; H\,O\,H \end{array} = \underset{\text{Urea.}}{CO(NH_2)_2} + \underset{\text{Sarcosine.}}{(CH_3)HN{\cdot}CH_2{\cdot}COOH}.$$

Creatinine, $C_4H_7N_3O$, is the anhydride of creatine—

$$\begin{array}{l} HN{:}C\text{—}N(CH_3){\cdot}CH_2 \\ \quad\;\; | \qquad\qquad\quad\;\; | \\ \quad NH\text{————}CO. \end{array}$$

Creatinine.

It is a normal constituent of urine, but the quantity is usually very small. It crystallises in colourless prisms, having a characteristic, lenticular form.

Among the better known amino-acids, found among the decomposition products of albuminoid substances, are **Alanine**, or α-amino-propionic acid, $CH_3{\cdot}CH(NH_2){\cdot}COOH$, a product of the decomposition of silk, and **Leucine**, or α-amino-isobutyl acetic acid, $(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO{\cdot}OH$, which is obtained, together with glycine and other substances by the decomposition of gelatine, glue, and other albuminoid substances by boiling them with mineral acids or caustic alkalis. Leucine is also formed during the digestion of proteins by trypsin, an enzyme derived from the pancreas.

3. Aldehydic and Ketonic Acids.

The Aldehydic and Ketonic Acids as their name implies, combine the properties of aldehydes or ketones with those of acids.

Glyoxalic Acid, *Glyoxylic acid*, $CHO{\cdot}CO{\cdot}OH + H_2O$, may be taken as the representative of an aldehydic acid. It is obtained by the oxidation of ethyl alcohol, glycol, or glycollic acid with nitric acid (p. 319), or by the reduction of oxalic acid on electrolysis or by means of magnesium powder.

Expt. 117.—Place 10 grams of magnesium powder in a flask, cover with water and cool well in ice. Then add 250 c.c. of a saturated

solution of oxalic acid. After it has stood for a time, filter. The solution may be used for the test for proteins (p. 598). Add a little glacial acetic and strong sulphuric acid to a few drops of it, and then a solution of egg-albumin; a violet coloration is produced.

Another method is to boil dichlor- or dibrom-acetic acid with water—

$$\underset{\text{Dichloracetic acid.}}{\begin{array}{l}CHCl_2\\ |\\ COOH\end{array}} + 2H_2O = \underset{\text{Intermediate product.}}{\begin{array}{l}CH(OH)_2\\ |\\ COOH\end{array}} + 2HCl = \underset{\text{Glyoxalic acid.}}{\begin{array}{l}CHO\\ |\\ COOH\end{array}} + H_2O.$$

The latter reaction resembles the formation of aldehyde from ethylidene chloride (p. 88). The acid is found in unripe fruits but disappears as the fruit ripens. It appears to be formed in small quantities when acetic acid is exposed to the air. Glyoxalic acid is usually obtained as a syrupy liquid which slowly crystallises on standing. It is very soluble in water and volatilises in steam. Whilst it forms salts with bases, it also reduces ammoniacal silver solution, producing a mirror, and reacts with hydroxylamine and phenylhydrazine like an aldehyde.

Pyruvic acid, $CH_3{\cdot}CO{\cdot}CO{\cdot}OH$, is the simplest of the ketonic acids. It is most readily prepared by distilling tartaric acid with acid potassium sulphate, which acts as a dehydrating agent.

$$\underset{\text{Tartaric acid.}}{C_4H_6O_6} = \underset{\text{Pyruvic acid.}}{C_3H_4O_3} + CO_2 + H_2O.$$

Pyruvic acid is a colourless liquid which boils at 165°. It yields lactic acid on reduction, and acetic acid and carbon dioxide on oxidation—

$$\begin{array}{l}CH_3\\ |\\ CH(OH)\\ |\\ COOH\end{array} \longleftarrow \begin{array}{l}CH_3\\ |\\ CO\\ |\\ COOH\end{array} \longrightarrow \begin{array}{l}CH_3\\ |\\ COOH\\ +\\ CO_2.\end{array}$$

Oxidation occurs readily on warming with an ammoniacal silver solution, the metal being deposited as a mirror. The reduction of silver nitrate solution is therefore not limited to aldehydes alone, but is brought about both by ketonic alcohols, like fructose (p. 296), and ketonic acids. The ketonic properties of the acid are exhibited in the compound which it forms with sodium bisulphite and the yellow crystalline phenylhydrazone, which is precipitated on adding a solution of phenylhydrazine acetate to the acid.

Acetoacetic Acid, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH$, is of little interest, but its ethyl ester (p. 188) has been extensively used for the synthesis of many ketones and acids. Ethyl acetoacetate is prepared as follows :—Metallic sodium, in thin slices, or as wire, is introduced into ten times its weight of pure ethyl acetate. The action, which begins slowly, becomes more vigorous after a time, and the liquid boils. The flask containing the mixture is then attached to an inverted condenser. To decompose the undissolved sodium, the liquid is finally heated on the water-bath. The sodium compound of ethyl acetoacetate is thus formed, from which dilute acetic acid liberates the ester as an oil, which floats on the surface of the liquid. The oil is removed and fractionated, the portion boiling at 175°–185° being separately collected.

Formation of Ethyl Acetoacetate.—The action of sodium on ethyl acetate has been carefully studied by Claisen, who has shown that the process is not a simple one, but involves four distinct reactions. Sodium only reacts in the presence of a little alcohol, with which it forms sodium alcoholate. The alcoholate is the active agent, uniting with a molecule of ethyl acetate to form an additive compound. The latter then reacts with a second molecule of ethyl acetate, forming the sodium compound of the new ester, and alcohol is then split off to form fresh sodium alcoholate with the metallic sodium. The addition of acetic acid replaces the sodium of the sodium compound by hydrogen. These reactions are represented as follows :—

1. $2C_2H_5OH + Na_2 = 2C_2H_5ONa + H_2.$

2. $$CH_3{\cdot}CO{\cdot}OC_2H_5 + NaOC_2H_5 = \underset{\text{Additive compound (not isolated)}}{CH_3C\begin{cases}ONa\\ OC_2H_5.\\ OC_2H_5\end{cases}}$$

3. $$CH_3{\cdot}C(ONa)(OC_2H_5)_2 + CH_3{\cdot}CO{\cdot}OC_2H_5$$
$$= \underset{\text{Sodium acetoacetic ester.}}{CH_3{\cdot}C(ONa){:}CH{\cdot}COOC_2H_5} + 2C_2H_5OH.$$

4. $$CH_3{\cdot}C(ONa){:}CH{\cdot}COOC_2H_5 + C_2H_4O_2$$
$$= \underset{\text{Acetoacetic ester.}}{CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5} + CH_3{\cdot}COONa.$$

The formula of the ester may also be written $CH_3{\cdot}C(OH){:}CH{\cdot}COOC_2H_5$. The double formula for acetoacetic ester represents a case of *Tautomerism*, which is discussed more fully on p. 330.

Properties of Ethyl Acetoacetate.—Ethyl acetoacetate is a colourless liquid with a fruity smell, which boils at 182°. It gives

a characteristic violet coloration with ferric chloride, and forms, on adding an aqueous alcoholic solution of cupric acetate to the ester, a crystalline copper compound which has the formula $(C_6H_9O_3)_2Cu$, corresponding to the sodium compound. Ethyl acetoacetate has a peculiar interest in organic chemistry from the extraordinary number and variety of synthetic products to which it gives rise. Its peculiar properties appear to be associated with the presence in its molecule of the grouping $-CO{\cdot}CH_2{\cdot}CO-$. We must confine our attention to a few of its more important properties.

Synthetic Uses of Acetoacetic Ester.—When the calculated quantity (1 atom) of sodium dissolved in alcohol (*i.e.* an alcoholic solution of sodium alcoholate) is added to acetoacetic ester, the sodium compound of the ester is formed. If an alkyl iodide is now boiled with the sodium compound, an alkyl derivative of acetoacetic ester is formed. In this way methyl iodide gives methyl acetoacetic ester—

$$\mathrm{CH_3{\cdot}C{\cdot}O\begin{array}{|c|}Na\\ I\end{array} : \underset{+\uparrow\ CH_3}{CH}{\cdot}COOC_2H_5 = CH_3{\cdot}CO{\cdot}\underset{\underset{\displaystyle CH_3}{|}}{CH}{\cdot}COOC_2H_5 + NaI.}$$

Methylacetoacetic ester.

A second atom of hydrogen of the acetoacetic ester may now be replaced by sodium as before, and by the action of another molecule of the alkyl iodide, a second alkyl group may be introduced. The alkyl group may be the same as the previous one or different. A second molecule of methyl iodide yields dimethylacetoacetic ester—

$$\mathrm{CH_3{\cdot}C{\cdot}O\begin{array}{|c|}Na\\ I\end{array} : \underset{+\uparrow\ CH_3}{C}(CH_3){\cdot}COOC_2H_5 = CH_3{\cdot}CO{\cdot}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{\cdot}COOC_2H_5 + NaI.}$$

Dimethylacetoacetic ester.

The two atoms of hydrogen cannot, however, be replaced simultaneously by sodium: the reaction must be performed in two steps, as described.

Acetoacetic ester and its alkyl derivatives undergo decomposition in two ways, according to whether dilute alkalis or acids or, on the other hand, strong alkalis are employed.

With *dilute* aqueous or alcoholic caustic alkalis or baryta, a ketone is formed (*ketonic hydrolysis*)—

$$\begin{array}{l} CH_3{\cdot}CO{\cdot}CH_2{\cdot}\vdots CO \vdots OC_2H_5 \\ \qquad\qquad + H \vdots O \vdots H \end{array} = \underset{\text{Acetone.}}{CH_3{\cdot}CO{\cdot}CH_3} + CO_2 + C_2H_5OH.$$

Concentrated alcoholic potash decomposes the ester into salts of 2 molecules of acid (*acid hydrolysis*)—

$$\begin{array}{l} CH_3{\cdot}CO{\cdot}\vdots CH_2{\cdot}CO \vdots OC_2H_5 \\ \quad + HO \vdots H + HO \vdots H \end{array} = CH_3{\cdot}CO{\cdot}OH + CH_3{\cdot}CO{\cdot}OH + C_2H_5OH.$$

If the alkyl derivatives of the ester are employed, it is possible to effect the synthesis of a series of ketones by the ketonic decomposition, or a series of fatty acids by the acid decomposition. Thus the monomethyl derivative of acetoacetic ester would yield, by the first process, methyl ethyl ketone; by the second, a mixture of acetic acid and propionic acid; whilst the dimethyl derivative would give, in the first case, methyl isopropyl ketone, and in the second a mixture of acetic and isobutyric acid. These are two of the most important synthetic processes for preparing ketones and acids, and should be included among the methods given on p. 129 and p. 154.

Dynamic Isomerism, *tautomerism.*—It has already been stated that, according to its mode of formation, the sodium compound of ethyl acetoacetate must be derived from an ester having the following formula, which is that of an unsaturated hydroxy-acid—

$$CH_3{\cdot}C(OH){:}CH{\cdot}COOC_2H_5,$$

whilst the various reactions enumerated above point to the formula of a ketonic ester—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5.$$

Two formulæ are therefore representative of the same substance. Which is correct?.

Our previous experience of the behaviour of the hydroxyl group in alcohols and acids towards metallic sodium would naturally suggest the hydroxyl form for the ester; but there is strong evidence in support of the ketone form. Thus, acetoacetic ester gives β-hydroxybutyric ester on reduction; that is, the ketone group becomes a secondary alcohol group—

$$\underset{\beta\text{-Hydroxybutyric ester.}}{CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}COOC_2H_5.}$$

Moreover, like a ketone, it reacts with phenylhydrazine and hydroxylamine. The liquid is in fact an equilibrium mixture of both forms, one or other form predominating according to the temperature and the action of different reagents. By freezing the liquid at − 79° the pure ketonic form has been obtained in the crystalline form, melting at − 39° C., and constitutes about 98 per cent. of the mixture. It gives the reactions of a ketone but no colour with ferric chloride, whereas the original compound gives a violet-red colour with this reagent, which is used as a qualitative test for the hydroxyl group. Separation of the hydroxylic or *enol* form has also been accomplished by fractional distillation of the liquid at low pressure in an apparatus made entirely of silica. Glass catalyses the conversion of the enol form to the ordinary equilibrium mixture.

Various names have been used to denote this kind of isomerism, in which a molecule is represented as a system of two different forms in self-adjusting equilibrium, thus—

$$-C(OH){:}CH \rightleftarrows -CO{\cdot}CH_2-$$

The terms tautomerism (ταὐτό, the same; μέρος, a part) and desmotropism (δεσμός, a bond; τρέπειν, to change) have been applied to this and similar cases, but since the *keto* and *enol* forms of ethylacetoacetate have now been separated, it seems to be better to class this peculiarly labile type of isomerism under the more comprehensive term of **dynamic isomerism**.

Levulinic Acid, *Acetylpropionic acid*, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}OH$, is formed by heating with dilute hydrochloric acid either the hexoses, or such substances as starch and cane-sugar which yield hexoses on hydrolysis. The product is filtered, evaporated and distilled *in vacuo*. Levulinic acid is a crystalline solid which melts at 33°. Neither the acid nor its ester forms a sodium compound like acetoacetic ester. The latter property is usually connected with the group $CO{\cdot}CH_2{\cdot}CO$ (p. 329), which is not present in levulinic acid.

Questions on Chapter XXI

1. Describe the methods of preparing the hydroxy-acids of the fatty series. Give some account of their properties.

2. What is the action of hydrogen cyanide on ketones and aldehydes? Mention two examples in which this action has been utilised in effecting the synthesis of important organic compounds.

3. Show how lactic acid may be produced from propionic acid and from acetaldehyde, and how these substances may be obtained from lactic acid.

4. Describe the properties of the hydroxy-acids. What is the action of phosphorus chloride, hydrobromic acid, hydriodic acid, and nitric acid on glycollic acid?

5. Several acids are known having the composition expressed by the formula $C_3H_6O_3$. Expand this into the several constitutional formulæ. What facts go to prove that lactic acid is both acid and alcohol?

6. Describe how α- and β-lactic acids may be obtained synthetically. What is the result of heating each variety? Which exhibits optical isomerism? Give a brief account of the theory which is generally accepted as accounting for this kind of isomerism.

7. Give an account of the behaviour of different kinds of hydroxy-acids on heating. Explain the theory which accounts for the formation of lactones.

8. What is meant by the term amino-acid? What are its properties? In what respect does it differ from an amide?

9. Describe the preparation of glycine. How can it be converted into glycollic acid?

10. What is hippuric acid? How is its constitution determined? Name any other derivatives of glycine obtained from natural sources, and gives their formulæ.

11. Give an example of an aldehydic and a ketonic acid, and describe some of their characteristic properties.

12. What is the action of sodium on ethyl acetate? Indicate how the resulting product may be made the means of obtaining (*a*) a substituted acetic acid, (*b*) a substituted acetone.

13. Describe and explain the formation of ethyl acetoacetate, and give an account of the various syntheses in which it has been employed.

14. Explain the meaning of the term *tautomerism*.

CHAPTER XXII

THE DIBASIC ACIDS AND THEIR DERIVATIVES

The Dibasic Acids contain two carboxyl groups and consequently two replaceable hydrogen atoms. According to whether one or both hydrogen atoms are replaced, they form acid and neutral salts and esters—in some cases salts with two different metals and salts containing a metal and an alkyl group. They may be regarded as paraffins in which two hydrogen atoms are substituted by carboxyl groups, or fatty acids in which one alkyl hydrogen is so replaced. Oxalic acid may be taken as representative of the group of dibasic acids. It forms the following series of compounds—

$\begin{array}{l} CO\cdot OH \\ \vert \\ CO\cdot OH \end{array}$	$\begin{array}{l} CO\cdot OH \\ \vert \\ CO\cdot OK \end{array}$	$\begin{array}{l} CO\cdot OK \\ \vert \\ CO\cdot OK \end{array}$	$\left[\begin{array}{l} CO\cdot O \\ \vert \\ CO\cdot O \end{array}\right]_2 \begin{array}{l} (K_2) \\ \\ Fe'' \end{array}$
Oxalic acid, or Dicarboxyl.	Potassium hydrogen oxalate.	Potassium oxalate.	Potassium ferrous oxalate.

$\begin{array}{l} CO\cdot OH \\ \vert \\ CO\cdot OC_2H_5 \end{array}$	$\begin{array}{l} CO\cdot OC_2H_5 \\ \vert \\ CO\cdot OC_2H_5 \end{array}$	$\begin{array}{l} CO\cdot OK \\ \vert \\ CO\cdot OC_2H_5. \end{array}$
Ethyl oxalic acid.	Diethyl oxalate.	Ethyl potassium oxalate.

The dibasic acids are colourless, crystalline substances (with the exception of carbonic acid, which is known only in the form of its salts and esters). They dissolve in water, to which they impart a strongly acid reaction. The lower members cannot be distilled without decomposition.

The following table contains a list of the more important members of the group :—

TABLE XIII.

THE DIBASIC ACIDS, $C_nH_{2n-2}O_4$.

		Melting-point.
Carbonic acid	$HO\cdot CO\cdot OH$	—
Oxalic acid	$COOH\cdot COOH$	189°
Malonic acid	$COOH\cdot CH_2\cdot COOH$	134°
Succinic acid	$COOH\cdot CH_2\cdot CH_2\cdot COOH$	182°
Glutaric acid	$COOH\cdot (CH_2)_3\cdot COOH$	97°
Adipic acid	$COOH\cdot (CH_2)_4\cdot COOH$	150°
Pimelic acid	$COOH\cdot (CH_2)_5\cdot COOH$	103°

Preparation of the Dibasic Acids.—The dibasic acids are prepared by processes which recall the formation of the fatty acids. The glycols with two primary alcohol groups yield dibasic acids on oxidation. Ethylene glycol forms oxalic acid—

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2O_2 = \begin{array}{l} CO{\cdot}OH \\ | \\ CO{\cdot}OH \end{array} + 2H_2O.$$
$$\text{Oxalic acid.}$$

The dicyanides form dibasic acids on hydrolysis. Cyanogen gas when dissolved in water and allowed to stand gives ammonium oxalate (p. 211). A third method is to form the cyanogen derivative of the fatty acid by acting upon the halogen substitution product with potassium cyanide and hydrolysing the product with alkali or mineral acids in the usual way. Monochloracetic acid can, in this way, be converted into cyanacetic acid and malonic acid—

$$\underset{\text{Chloracetic acid.}}{\begin{array}{l} CH_2Cl \\ | \\ CO{\cdot}OH \end{array}} \xrightarrow{KCN} \underset{\text{Cyanacetic acid.}}{\begin{array}{l} CH_2{\cdot}CN \\ | \\ CO{\cdot}OH \end{array}} \xrightarrow{H_2O} \underset{\text{Malonic acid.}}{\begin{array}{l} CH_2{\cdot}CO{\cdot}OH \\ | \\ CO{\cdot}OH \end{array}}$$

An interesting method for preparing the higher dibasic acids is by the electrolysis of the potassium alkyl salts of the lower dibasic acids. Potassium ethyl malonate, on electrolysis, decomposes in the following way—

$$\begin{array}{l} C_2H_5O{\cdot}CO{\cdot}CH_2{\cdot} \vdots CO{\cdot}O \vdots K \\ C_2H_5O{\cdot}CO{\cdot}CH_2{\cdot} \vdots CO{\cdot}O \vdots K \end{array} = \underset{+\text{ Electrode.}}{\begin{array}{l} C_2H_5O{\cdot}CO{\cdot}CH_2 \\ \qquad\qquad\quad | \\ C_2H_5O{\cdot}CO{\cdot}CH_2 \end{array}} + \begin{array}{l} CO_2 \\ CO_2 \end{array} + \underset{-\text{ Electrode.}}{\begin{array}{l} K \\ K \end{array}}$$

The product is the higher homologue, succinic ester, which separates at the positive electrode; the reaction resembles the production of ethane from potassium acetate (p. 153).

Carbonic Acid, HO·CO·OH.—Apart from the fact that the salts and esters of carbonic acid contain only one carboxyl group, the compounds are those of a dibasic acid. The metallic salts are usually described among the metals in text-books of inorganic chemistry. The alkyl esters are obtained by boiling silver carbonate

with the alkyl iodide. Ethyl iodide forms ethyl carbonate, which is a liquid, boiling at 126°—

$$OC\begin{cases} O\,Ag \quad I\,C_2H_5 \\ \qquad + \\ O\,Ag \quad I\,C_2H_5 \end{cases} = \underset{\text{Ethyl carbonate.}}{OC(OC_2H_5)_2} + 2AgI.$$

On passing carbon dioxide into alcoholic potash, the potassium alkyl carbonate is precipitated as a white crystalline powder. Ethyl alcoholic potash gives ethyl potassium carbonate—

$$C_2H_5OH + KOH + CO_2 = \underset{\substack{\text{Ethyl potassium} \\ \text{carbonate.}}}{OC\begin{cases} OC_2H_5 \\ OK \end{cases}} + H_2O.$$

EXPT. 118.—Boil powdered caustic potash with ethyl alcohol on the water-bath, cool, and decant the clear solution. Pass a rapid current of carbon dioxide through the solution. The crystalline ethyl potassium carbonate is rapidly precipitated with evolution of heat.

Carbonyl Chloride,[1] *Carbon oxychloride, Phosgene,* is obtained by the direct union of carbon monoxide and chlorine in sunlight. The discovery is due to J. Davy (1811), who gave the name phosgene (φῶς, light; γεννάω, I produce) to the gas to describe its mode of production. Carbonyl chloride is also formed by the oxidation of chloroform in presence of oxygen and light (p. 90), or by the aid of potassium dichromate and sulphuric acid. It is most conveniently prepared on a small scale by the action of sulphur trioxide on carbon tetrachloride, $CCl_4 + 2SO_3 = COCl_2 + SO_2Cl_2{\cdot}SO_3$.

Great care must be taken in preparing it, as it is extremely poisonous and has been used as a poison gas in warfare. Its harmful action is usually delayed, and is attributed to the slow hydrolysis of the gas by moisture in the lungs. The preparation in the laboratory should not be attempted without using special precautions.

Phosgene is produced on the large scale by passing a mixture of carbon monoxide and chlorine through charcoal, combination between the gases being effected by contact action, or catalysis. Carbonyl chloride is used in the manufacture of certain organic

[1] The term *carbonyl*, or *carbonyl group*, stands for the radical CO.

colouring matters (p. 523) and for the preparation of a variety of other synthetic products (pp. 336, 486). It readily condenses to a liquid at 8° and has a peculiarly suffocating and pungent smell. The solution of the gas in benzene or toluene, which absorb as much as 20 per cent. of carbonyl chloride, is convenient for experimental purposes. Carbonyl chloride has the properties of an acid chloride, and may be regarded as the acid chloride of carbonic acid. The gas fumes in moist air, decomposing into hydrochloric acid and carbon dioxide—

$$OC\begin{array}{l}\diagup Cl \\ \diagdown Cl\end{array} + \begin{array}{l} H\,OH \\ H\,OH\end{array} = CO_2 + 2HCl + H_2O.$$

It reacts with bases like ammonia and aniline to give urea or a derivative of urea—

$$OC\begin{array}{l}\diagup Cl \\ \diagdown Cl\end{array} + \begin{array}{l} H\,NH_2 \\ H\,NH_2\end{array} = \underset{\text{Urea.}}{OC\begin{array}{l}\diagup NH_2 \\ \diagdown NH_2\end{array}} + 2HCl$$

$$OC\begin{array}{l}\diagup Cl \\ \diagdown Cl\end{array} + \underset{\text{Aniline.}}{\begin{array}{l} H\,NH{\cdot}C_6H_5 \\ H\,NH{\cdot}C_6H_5\end{array}} = \underset{\text{Diphenyl urea.}}{OC\begin{array}{l}\diagup NH{\cdot}C_6H_5 \\ \diagdown NH{\cdot}C_6H_5\end{array}} + 2HCl$$

It is also decomposed by alcohol, and gives chloroformic ester according to the following equation—

$$OC\begin{array}{l}\diagup Cl \\ \diagdown Cl + H\,OC_2H_5\end{array} = \underset{\text{Chloroformic ester.}}{OC\begin{array}{l}\diagup Cl \\ \diagdown OC_2H_5\end{array}} + HCl.$$

Chloroformic ester, $Cl{\cdot}COOC_2H_5$, the ester of an unknown acid, is used as a convenient reagent for introducing the ester group $-COOC_2H_5$ into organic compounds. Thus the sodium derivative of ethyl acetoacetate (p. 328) reacts with chloroformic ester, as follows—

$$\begin{array}{l}CH_3{\cdot}C{:}CH{\cdot}COOC_2H_5 \\ \quad\;\; | \\ \quad\; ONa\end{array} + Cl{\cdot}COOC_2H_5 = \begin{array}{l}CH_3{\cdot}C{:}CH{\cdot}COOC_2H_5 \\ \quad\;\; | \\ \quad\; O{\cdot}COOC_2H_5\end{array} + NaCl$$

Urethane, *Ethyl carbamate,* $NH_2{\cdot}CO{\cdot}OC_2H_5$, is the product formed by the action of ammonia on chloroformic ester, and is used as a hypnotic—

$$OC\begin{cases}\boxed{Cl + H}NH_2\\OC_2H_5\end{cases} + NH_3 = \underset{\text{Urethane.}}{OC\begin{cases}NH_2\\OC_2H_5\end{cases}} + NH_4Cl.$$

A variety of similar hypnotics are produced by replacing the amino-group by substituted amino-groups and ethoxy-groups by other alkoxy-radicals. *Hedonal,* $NH_2{\cdot}COOC_5H_{11}$, is an example. Hedonal has also been used as an anæsthetic.

Urethane is the ethyl ester of carbamic acid. The acid itself is unknown in the free state, but the ammonium salt is a common constituent of commercial ammonium carbonate. Ammonium carbamate is readily obtained by passing carbon dioxide into an alcoholic solution of ammonia—

$$2NH_3 + CO_2 = OC\begin{cases}NH_2\\ONH_4.\end{cases}$$

EXPT. 120.—Pass ammonia gas into ethyl alcohol until the alcohol is saturated, then bubble carbon dioxide through the liquid. Ammonium carbamate is precipitated in the form of a white crystalline powder.

Urea, *Carbamide,* $CO(NH_2)_2$.—When ammonia is added to carbonyl chloride, urea is formed (p. 336), just as acetamide is obtained when ammonia acts upon acetyl chloride (p. 177).

This reaction determines the constitution of urea, as the amide of carbonic acid. Hence the name carbonic amide, or shortly *carbamide,* which is synonymous with urea.

That the substance is an amide is further seen from its behaviour with boiling caustic alkalis, which decompose it into ammonia and a salt of carbonic acid (p. 180)—

$$OC\begin{cases}NH_2\\NH_2\end{cases} + 2NaOH = Na_2CO_3 + 2NH_3.$$

The presence of amino-groups is also shown by the action of nitrous acid, which liberates nitrogen; at the same time carbon dioxide is evolved—

$$\begin{array}{l} \mathrm{HO}\ \ \mathrm{N}\,\mathrm{O} \\ \quad + \\ \mathrm{CO}\left\langle \begin{array}{l} \mathrm{N}\,\mathrm{H_2} \\ \\ \mathrm{N}\,\mathrm{H_2} \end{array}\right. = CO_2 + H_2O + 2N_2 + 2H_2O. \\ \quad + \\ \mathrm{HO}\ \ \mathrm{N}\,\mathrm{O} \end{array}$$

EXPT. 121.—Add to a solution of urea in water a little sodium nitrité solution and a few drops of hydrochloric acid. Effervescence occurs and nitrogen and carbon dioxide are evolved.

It is now prepared commercially as a fertiliser by heating carbon dioxide with ammonia under pressure—

$$CO_2 + 2NH_3 = CO(NH_2)_2 + H_2O.$$

Urea is a colourless substance which crystallises in long prisms, melting at 132°. It is very soluble in water and in hot alcohol. When heated, it decomposes into ammonia, biuret (see below), and cyanuric acid. It is used in making plastic resins (p. 137).

The chief interest attaching to urea is its presence in normal human urine, about 30 grams being excreted daily. Urea may be regarded as the final decomposition product of the waste nitrogenous materials of the body. It is obtained from urine by concentration and extraction with alcohol, which dissolves out the urea. The alcoholic extract is allowed to evaporate and the urea then crystallises.

When urine is exposed to the air, fermentation sets in by the action of an enzyme, *urease*, the urea being converted into ammonia and carbon dioxide—

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3.$$

Detection and Estimation of Urea.—The presence of urea may be detected by a variety of reactions, which are described in the following experiments :—

EXPT. 122.—1. Heat a few crystals of urea over a very small flame until they melt and slowly evolve bubbles of ammonia gas. Continue to heat for a minute or two, then cool and add a few drops of water, a drop or two of copper sulphate solution, and finally caustic soda solution, until a clear solution is obtained. A violet, or pink, solution

is produced, from a compound of *biuret* with copper. The formation of biuret from urea takes place according to the following equation—

$$\underset{\text{Urea.}}{NH_2{\cdot}CO{\cdot}NH}\boxed{H + NH_2}\underset{\text{Urea.}}{{\cdot}CO{\cdot}NH_2} = \underset{\text{Biuret.}}{NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2} + NH_3.$$

Two molecules of urea combine with the elimination of one molecule of ammonia.

2. Add to a solution of urea a few drops of a neutral solution of mercuric nitrate. A white curdy precipitate is thrown down, which is a basic compound of mercuric nitrate and urea—

$$[CO(NH_2)_2]_2{\cdot}Hg(NO_3)_2{\cdot}3HgO.$$

3. Add to a strong solution of urea in water a few drops of strong nitric acid, and to another portion a strong solution of oxalic acid. In one case urea nitrate and in the other urea oxalate is precipitated in crystals which have a characteristic appearance under the microscope—

$$\underset{\text{Urea nitrate.}}{CO(NH_2)_2{\cdot}HNO_3} \qquad \underset{\text{Urea oxalate.}}{[CO(NH_2)_2]_2C_2H_2O_4 + H_2O.}$$

4. Add to a solution of urea a few drops of an alkaline solution of sodium hypochlorite or hypobromite. Effervescence occurs, and free nitrogen is evolved, the alkali retaining the carbon dioxide, which is liberated at the same time—

$$\begin{array}{cccccc} & \boxed{H_2}N— & & \boxed{CO}— & & N\boxed{H_2} \\ & + & & + & & + \\ Na & \boxed{O}Cl & Na & \boxed{O}Cl & Na & \boxed{O}Cl \end{array} = 3NaCl + 2H_2O + CO_2 + N_2.$$

This reaction is utilised for the quantitative estimation of urea in urine. It may be performed by the aid of Lunge's nitrometer (Fig. 81). A solution of sodium hypobromite is prepared by dissolving 100 grams of caustic soda in 250 c.c. of water and adding 25 c.c. of bromine.

25 c.c. of this solution is introduced into the flask *a* together with a small tube containing 5 c.c. of urine. The graduated vessel *b* is filled with water by raising the reservoir *c*. The pressure in the flask is adjusted by turning the three-way tap *d* so that the vessel is for a moment in communication with the air. The tap is then turned so that a connection is made between the flask and the graduated tube, and the small tube containing the urine is then allowed to drop into the hypobromite solution. Nitrogen is evolved, and the liquid in *b* descends. When gas ceases to be evolved, the pressure in the graduated tube is adjusted by means of the reservoir, and the volume of gas is read off. The volume of gas corresponding to the urea present is always about 8 per cent. below the theoretical amount, and a correction

to this extent must be introduced. A more convenient apparatus is known as *Doremus' ureometer* (Fig. 82). The wide vertical tube is filled with the solution of sodium hypobromite prepared as described above, whilst the narrow side-tube is charged with the urine or urea solution. The tap is carefully opened and 1 c.c. of the urea solution allowed to flow in; gas is evolved and the volume read off. In analysing urine it is customary to estimate, in addition to the urea, the total nitrogen by Kjeldahl's method.

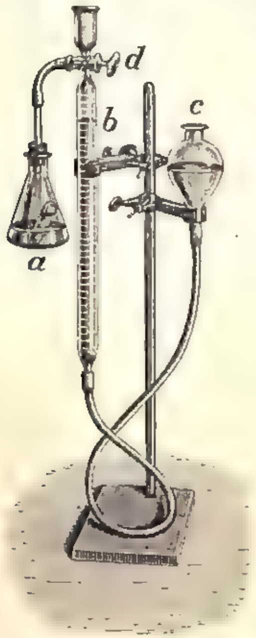


FIG. 81.—Lunge's Nitrometer for the estimation of Urea.

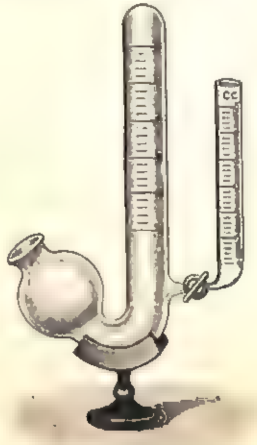


FIG. 82.

5. More accurate results are obtained by decomposing urea by means of the enzyme *urease* (p. 338), which is present in soya beans, and the estimation is easily carried out. 25 c.c. of a 2 per cent. aqueous solution of urea are placed in a flask, together with about 5 grams of powdered soya beans. The flask is fitted with a stopper and delivery tube, similar to that used in Kjeldahl's estimation of nitrogen (Fig. 20, p. 26), except that provision should be made for drawing a slow current of air through the apparatus and the flask is warmed in a water-bath to 40° C. instead of by a bunsen burner. The urea is decomposed into carbon dioxide and ammonia, which are drawn by the current of air into a measured volume of standard sulphuric acid. After passing the air for about an hour, the contents of the reaction flask are made alkaline with a solution of sodium carbonate and the current of air is

allowed to pass for another half-hour. The excess of standard acid is then determined by titration with standard alkali, and from the result the amount of ammonia liberated from the urea can be calculated.

The transformation of ammonium cyanate into urea as described on p. 221 is the reaction which Wöhler used in 1828, and which is the first authentic case on record of the artificial synthesis of a so-called organic compound. Further study has shown that the rearrangement of the molecules is a reversible action, the solution at equilibrium containing chiefly urea, together with a little ammonium isocyanate. It has also been suggested that urea itself exhibits dynamic isomerism (p. 330), and recent work on its molecular configuration by X-ray analysis lends support to the view that a small proportion exists in the form of $HO{-}C\begin{matrix}\diagup NH_2\\ \diagdown NH\end{matrix}$.

Cyanamide, $NC{\cdot}NH_2$, is prepared by the action of mercuric oxide on thiourea, which removes from the latter hydrogen sulphide—

$$\underset{\text{Thiourea.}}{SC(NH_2)_2} - H_2S = \underset{\text{Cyanamide.}}{N{\vdots}C{\cdot}NH_2}.$$

The disodium and calcium compounds are formed as intermediate products in the manufacture of sodium cyanide from sodamide and of calcium cyanide from the carbide (p. 214)—

$$2NaNH_2 + C = \underset{\substack{\text{Disodium}\\ \text{cyanamide.}}}{CN{\cdot}NNa_2} + 2H_2.$$

$$CaC_2 + N_2 = \underset{\text{Calcium cyanamide.}}{NC{\cdot}NCa} + C$$

Cyanamide is a colourless, deliquescent substance, which melts at 40° and is soluble in water and alcohol. By the action of mineral acids it takes up water and forms urea. The reaction resembles the formation of formamide from hydrocyanic acid (p. 213)—

$$NH_2{\cdot}CN + H_2O = OC(NH_2)_2.$$

The calcium compound or *nitrolime* has been found useful as a manure in place of nitrates and ammonium salts.

Guanidine, $(NH_2)_2C{:}NH$.—Ammonia combines with cyanamide and forms guanidine—

$$NH_2{\cdot}CN + NH_3 = \underset{\text{Guanidine.}}{NH_2{\cdot}C\begin{matrix}\diagup\!\!\diagup NH\\ \diagdown NH_2\end{matrix}}.$$

It is more conveniently prepared by heating ammonium thiocyanate (p. 223) to 180°. The formation of guanidine depends on that of thiourea and cyanamide as intermediate products. Cyanamide combines with ammonium thiocyanate to produce the thiocyanate of guanidine—

$$\left.\begin{array}{l}\quad(NH_4)SCN \\ \quad\swarrow \\ SC(NH_2)_2 \rightarrow NH_2CN\end{array}\right\} = \underset{\text{Guanidine thiocyanate.}}{NH_2{\cdot}C{:}NH{\cdot}NH_2{\cdot}HSCN.}$$

Guanidine is a deliquescent, crystalline compound with strongly alkaline properties, which combines with carbon dioxide and other acids, forming crystalline salts. Guanidine is found among the products of oxidation of certain protein substances, such as egg-albumin and the albumin of lupine seedlings, as well as of guanine (p. 373). Guanidine may be regarded as a constituent of creatine (p. 326). It is intimately associated with the nitrogenous products of the animal and vegetable organism.

Semicarbazide, $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ is an important reagent for the characterisation of aldehydes and ketones. It may be obtained from guanidine, which is first nitrated to *nitroguanidine*, $NH{:}C\begin{cases}NH_2\\NH{\cdot}NO_2\end{cases}$. The latter is then reduced with zinc dust and acetic acid to *aminoguanidine*, $HN{:}C\begin{cases}NH_2\\NH{\cdot}NH_2\end{cases}$, which is hydrolysed when warmed with acids to give ammonia and semicarbazide—

$$HN{:}C\begin{cases}NH_2\\NH{\cdot}NH_2\end{cases} + H_2O = NH_3 + \underset{\text{Semicarbazide.}}{O{:}C\begin{cases}NH_2\\NH{\cdot}NH_2\end{cases}}.$$

Semicarbazide reacts with aldehydes and ketones, to give crystalline semicarbazones, thus :

$$\begin{matrix}CH_3\\CH_3\end{matrix}\Big\rangle C{:}O + H_2N{\cdot}NH{\cdot}CO{\cdot}NH_2 = \underset{\text{Acetone semicarbazone.}}{\begin{matrix}CH_3\\CH_3\end{matrix}\Big\rangle C{:}N{\cdot}NH{\cdot}CONH_2} + H_2O.$$

The acetone semicarbazone, when recrystallised from alcohol, melts at 186° C.

Oxalic Acid, $CO{\cdot}OH{\cdot}CO{\cdot}OH + 2H_2O$.—Oxalic acid is found in wood sorrel (*Oxalis acetosella*) and other plants, as the acid potassium salt. The salt is sometimes called *salts of sorrel*. The calcium

salt is frequently found crystallised in plant cells. Certain lichens growing on limestone consist largely of this salt. It is also present in urine and in urinary calculi. It is produced by a peculiar fermentation of sugar caused by certain species of yeast and fungi. Scheele, in 1776, first obtained oxalic acid artificially by heating sugar with nitric acid.

EXPT. 123.—Pour 180 c.c. of strong nitric acid into a large flask (2 litres) and warm the acid on the water-bath. Remove the flask to the fume cupboard and add 50 grams of cane-sugar. Torrents of brown fumes are evolved. When the reaction has ceased, evaporate the liquid on the water-bath to one-quarter its bulk. On cooling, large, colourless, prismatic crystals of oxalic acid separate.

Oxalic acid is at present manufactured from sodium formate (p. 159)—

$$\underset{\text{Sodium formate.}}{2HCOONa} = \underset{\text{Sodium oxalate.}}{C_2O_4Na_2} + H_2.$$

EXPT. 124.—Heat a few grams of sodium formate in a test-tube. The gas which is evolved can be ignited at the mouth of the tube. If the residue is dissolved in water and filtered, the solution gives the reactions for oxalic acid (see below).

It is also obtained commercially from pine sawdust which is oxidised by fusion with caustic alkalis. The sawdust is stirred into a stiff paste with a mixture of strong caustic potash and soda solution, and the paste is heated on iron plates. The temperature is gradually raised, care being taken to avoid charring. The dry, brown mass is lixiviated with a small quantity of warm water which removes the excess of alkali and leaves the less soluble sodium oxalate. The waste alkali is recovered and used again. The sodium oxalate is dissolved in water, and converted into the insoluble lime salt by boiling with milk of lime, and the lime salt is separated and decomposed with sulphuric acid. The liquid, separated from the calcium sulphate, is evaporated, when the oxalic acid crystallises in long prisms, containing two molecules of water of crystallisation. When a solution of cyanogen in water is allowed to stand for some time, slow hydrolysis takes place, and among the products formed is ammonium oxalate (p. 211), so that cyanogen is the dinitrile of oxalic acid.

Properties of Oxalic Acid.—Oxalic acid crystallises in long, colourless prisms containing two molecules of water of crystallisation. When heated to 100°, the water of crystallisation is driven off. Above this temperature part of the acid melts, a part sublimes, and a certain amount decomposes into carbon dioxide and formic acid. When warmed with strong sulphuric acid, oxalic acid breaks up into carbon dioxide and carbon monoxide—

$$C_2O_4H_2 - H_2O = CO_2 + CO.$$

EXPT. 125.—Heat a few grams of oxalic acid, or an oxalate, with an equal bulk of strong sulphuric acid. Effervescence ensues without charring, and the gas, which is evolved, may be ignited.

Oxalic acid, in presence of dilute sulphuric acid, is rapidly oxidised by potassium permanganate, on warming, to carbon dioxide and water. The process is utilised in volumetric analysis.

$$5C_2O_4H_2 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + 8H_2O + K_2SO_4 + 2MnSO_4.$$

EXPT. 126.—Dissolve a few crystals of oxalic acid, or an oxalate in water; add dilute sulphuric acid and warm gently. Add potassium permanganate, drop by drop. It is at first decolorised; but when the oxalic acid is all oxidised the pink colour remains.

Phosphorus pentachloride converts oxalic acid into *oxalyl chloride*. It is a colourless liquid which boils at 64°—

$$C_2H_2O_4 + 2PCl_5 = \underset{\text{Oxalyl chloride.}}{C_2O_2Cl_2} + 2POCl_3 + 2HCl.$$

Salts of Oxalic Acid.—The following are the most important salts of oxalic acid. Potassium oxalate, $C_2O_4K_2 + H_2O$, is soluble in water; the acid salt, C_2O_4HK, is less soluble and has been referred to as a constituent of many plants. Acid potassium oxalate combines with oxalic acid and forms what is known as potassium quadroxalate, $C_2O_4HK \cdot C_2H_2O_4 + 2H_2O$, which is sometimes used for removing ink-stains and iron-moulds, under the name of salts of sorrel, or lemon. The calcium salt, C_2O_4Ca, is found in plants; the precipitated salt, which is thrown down when calcium chloride is added to a solution of an oxalate, contains one molecule of water of crystallisation. Ferrous oxalate, $C_2O_4Fe + 2H_2O$, is precipitated as an insoluble, yellow powder when a ferrous salt is added to an oxalate on solution. Potassium ferrous oxalate,

$(C_2O_4)_2K_2Fe + H_2O$, has strong reducing properties, and is used as a developer in photography. It is obtained by mixing solutions of ferrous sulphate and potassium oxalate in certain proportions. The ferric alkali salts are green. The esters of oxalic acid are obtained by boiling the alcohol with anhydrous oxalic acid and distilling the product. *Methyl oxalate* is a solid, which melts at 51° and boils at 162°; *ethyl oxalate* is a liquid boiling at 186°. Both esters are rapidly hydrolysed by alkalis in the cold. Oxalic acid and its soluble salts are very poisonous.

Oxamide, $CONH_2{\cdot}CONH_2$, is obtained by heating ammonium oxalate, or, more readily, by adding strong ammonia to methyl, or ethyl, oxalate, when oxamide is precipitated as a white crystalline powder (p. 187)—

$$\begin{array}{l} CO{\cdot}OC_2H_5 \\ | \\ CO{\cdot}OC_2H_5 \end{array} + 2NH_3 = \underset{\text{Oxamide.}}{\begin{array}{l} CO{\cdot}NH_2 \\ | \\ CO{\cdot}NH_2 \end{array}} + 2C_2H_5OH.$$

Oxamide is converted on the one hand into cyanogen, by heating with phosphorus pentoxide; and on the other into oxalic acid and ammonia, by hydrolysis with alkalis—

$$\begin{array}{l} CN \\ | \\ CN \end{array} \xleftarrow{-2H_2O} \begin{array}{l} CO{\cdot}NH_2 \\ | \\ CO{\cdot}NH_2 \end{array} \xrightarrow{+2H_2O} \begin{array}{l} CO{\cdot}OH \\ | \\ CO{\cdot}OH \end{array} + \begin{array}{l} NH_3 \\ \\ NH_3. \end{array}$$

EXPT. 127.—Bring into a hard glass test-tube some phosphorus pentoxide to a depth of about ½ inch and immediately add about half its bulk of oxamide. Mix thoroughly by shaking and stirring with a glass rod, and then heat. The cyanogen can be ignited at the mouth of the tube.

Malonic Acid, $CH_2(CO{\cdot}OH)_2$, is found as the calcium salt in beet-root. It was originally prepared by the oxidation of malic acid (p. 352) with potassium dichromate and sulphuric acid, a process which gave rise to the name; but it is now usual to obtain it from monochloracetic acid. Potassium chloracetate is boiled with potassium cyanide. The cyanacetate of potassium is then hydrolysed with strong hydrochloric acid; the product is evaporated to dryness and extracted with ether. When the ether has evaporated, malonic acid remains.

$$\begin{array}{l} CH_2Cl \\ | \\ CO_2K \end{array} + KCN = \begin{array}{l} CH_2CN \\ | \\ CO_2K \end{array} + KCl.$$

$$\begin{array}{l} CH_2CN \\ | \\ CO_2K \end{array} + 2H_2O + 2HCl = \begin{array}{l} CH_2{\cdot}CO_2H \\ | \\ CO_2H \end{array} + NH_4Cl + KCl.$$

It is a colourless, crystalline substance, which melts at 132°, and dissolves readily in water, alcohol, and in ether.

Malonic acid loses carbon dioxide on heating to 140°–150°, whereby it is converted into acetic acid. This is a characteristic property of all polybasic acids having two carboxyl groups attached to the same carbon atom.

$$\underset{\text{Malonic acid.}}{\begin{array}{l} CH_2{\cdot}COOH \\ | \\ COOH \end{array}} = \underset{\text{Acetic acid.}}{\begin{array}{l} CH_3 \\ | \\ COOH \end{array}} + CO_2.$$

EXPT. 128.—Heat a little malonic acid in a test-tube until it melts and effervesces, and decant the gas given off into lime-water. The presence of carbon dioxide is shown by the turbidity of the lime-water, whilst the liquid which remains has the smell of acetic acid.

When malonic acid is heated with phosphorus pentoxide a gas escapes which can be condensed to a solid in liquid air. It has the formula C_3O_2, and is termed carbon suboxide. It is formed according to the equation—

$$CH_2(COOH)_2 - 2H_2O = C_3O_2.$$

It re-unites with water to form malonic acid and with ammonia to form malonamide, and probably has the constitution—

$$C\begin{array}{l} \nearrow\!\!\!\!\nearrow CO \\ \searrow\!\!\!\!\searrow CO \end{array}.$$

Malonic ester is prepared from cyanacetic acid by heating it with a mixture of alcohol and sulphuric acid. The hydrolysis of the cyanogen group to carboxyl and the formation of the ester proceed simultaneously—

$$\underset{\text{Cyanacetic acid.}}{\begin{array}{l} CH_2CN \\ | \\ COOH \end{array}} \longrightarrow \underset{\text{Malonic acid.}}{\begin{array}{l} CH_2{\cdot}COOH \\ | \\ CO{\cdot}OH \end{array}} \longrightarrow \underset{\text{Diethyl malonate.}}{\begin{array}{l} CH_2{\cdot}COOC_2H_5. \\ | \\ CO{\cdot}OC_2H_5. \end{array}}$$

The esters are fragrant-smelling liquids, which are insoluble in water and can be distilled.

EXPT. 128*a*.—*Preparation of Malonic Ester.*—Dissolve 25 grams of monochloracetic acid in 50 c.c. of water in a large basin, which is gently warmed on a sand-bath in the fume chamber, and stir slowly into the solution about 15 grams of anhydrous sodium carbonate until the reaction is just alkaline and the carbon dioxide has all been liberated. The temperature should not be allowed to rise above 60° C. during the neutralisation. Then remove the flame and stir 17 grams of potassium cyanide into the mixture. Great care should be taken to keep the mortar covered with a cloth while powdering the potassium cyanide. The mixture is again heated slowly with constant stirring, until the temperature reaches 135° C., at which level it should be kept for half an hour. Effervescence occurs and the mixture thickens. On cooling, it solidifies to a hard cake. This is powdered and mixed with 20 c.c. of alcohol in a round-bottomed flask. A cold mixture of 40 c.c. of concentrated sulphuric acid and an equal amount of alcohol are added with constant shaking, the flask being cooled in water. It is then heated under a reflux condenser on a water-bath for an hour and a half. The mixture is then poured into 250 c.c. of cold water and the solution is filtered and extracted with ether. The ethereal extract is washed two or three times with a dilute solution of sodium carbonate and then with water, and dried with anhydrous sodium sulphate. The clear solution is then decanted into a dry distilling flask, and after distilling off the ether, the crude oil is fractionally distilled. The pure oil distils at 198° C. A pure product can be obtained by distilling it under reduced pressure.

It is a colourless oil with a faint, fruity smell, and is slightly soluble in water. It is much used in the syntheses of fatty acids and other compounds.

Synthetic Uses of Malonic Ester.—Malonic ester shares the property of acetoacetic ester in forming a sodium compound when a solution of sodium alcoholate in alcohol is added to the ester (p. 328)—

$$\underset{\text{Malonic ester.}}{CH_2(COOC_2H_5)_2} + NaOC_2H_5 = \underset{\text{Sodium malonic ester.}}{CHNa(CO{\cdot}OC_2H_5)_2} + C_2H_5OH.$$

Cyanacetic ester behaves similarly.

This property is associated with the groups $CO{\cdot}CH_2{\cdot}CO$ and $CO{\cdot}CH_2{\cdot}CN$; that is to say, a methylene group, situated between ketone, cyanogen or certain other acidic groups—

$$\begin{array}{l} CO\cdot OC_2H_5 \\ | \\ CH_2 \\ | \\ CO\cdot OC_2H_5 \end{array} \qquad \begin{array}{l} CO\cdot CH_3 \\ | \\ CH_2 \\ | \\ CO\cdot OC_2H_5 \end{array} \qquad \begin{array}{l} CN \\ | \\ CH_2 \\ | \\ CO\cdot OC_2H_5. \end{array}$$

Malonic ester. Acetoacetic ester. Cyanacetic ester.

If the equivalent of one molecule of alkyl iodide is added to the sodium compound of malonic ester in alcoholic solution, and the mixture boiled, sodium iodide separates, and at the same time the alkyl malonic ester is formed. Methyl iodide gives methyl malonic ester. The product is poured into water, and the ester, which is insoluble, is separated and distilled—

$$\begin{array}{l} CH\,Na\,(CO\cdot OC_2H_5)_2 \\ + CH_3\,I \end{array} = \underset{\text{Methyl malonic ester.}}{CH_3\cdot CH(CO\cdot OC_2H_5)_2} + NaI.$$

A second alkyl group (it may be the same, or a different one), can then be introduced by repeating the above operation. Methyl iodide will give dimethyl malonic ester—

$$\begin{array}{l} CH_3\cdot C\,Na\,(CO\cdot OC_2H_5)_2 \\ + CH_3\,I \end{array} = \underset{\text{Dimethyl malonic ester.}}{(CH_3)_2C(CO\cdot OC_2H_5)_2}.$$

Ethyl iodide forms methyl ethyl malonic ester—

$$\begin{array}{l} CH_3\cdot C\,Na\,(CO\cdot OC_2H_5)_2 \\ + C_2H_5\,I \end{array} = \underset{\text{Methyl ethyl malonic ester.}}{\begin{array}{l} CH_3 \\ C_2H_5 \end{array}\!\!\!>C(CO\cdot OC_2H_5)_2}.$$

If the above esters are now hydrolysed with caustic potash and the free acids separated by the addition of hydrochloric acid and extraction with ether, new dibasic acids are obtained. The method is therefore important for obtaining *homologues of malonic acid*. As all the acids necessarily have, like malonic acid, two carboxyl groups linked to the same carbon atom, they lose carbon dioxide on heating, and pass into monobasic acids; methyl malonic acid gives propionic acid; dimethyl malonic acid forms isobutyric acid; methyl ethyl malonic acid produces methyl ethyl acetic acid—

$$\underset{\text{Methyl malonic acid.}}{CH_3{\cdot}CH(COOH)_2} = \underset{\text{Propionic acid.}}{CH_3{\cdot}CH_2{\cdot}COOH} + CO_2.$$

$$\underset{\text{Dimethyl malonic acid.}}{(CH_3)_2C(COOH)_2} = \underset{\text{Isobutyric acid.}}{(CH_3)_2{\cdot}CH{\cdot}COOH} + CO_2.$$

$$\underset{\text{Methyl ethyl malonic acid.}}{\begin{array}{l}CH_3\\C_2H_5\end{array}\!\!>C(COOH)_2} = \underset{\text{Methyl ethyl acetic acid.}}{\begin{array}{l}CH_3\\C_2H_5\end{array}\!\!>CH{\cdot}COOH} + CO_2.$$

In this way the *fatty acids may be synthesised.*

Malonic ester may also be employed in the *synthesis of saturated ring compounds* referred to on p. 256. To give one illustration: ethylene bromide and di-sodium malonic ester yield trimethylene dicarboxylic ester—

$$\begin{array}{l}CH_2Br\\|\\CH_2Br\end{array} + Na_2C(COOC_2H_5)_2 = \underset{\text{Trimethylene dicarboxylic ester.}}{\begin{array}{l}CH_2\\|\\CH_2\end{array}\!\!>C(COOC_2H_5)_2} + 2NaBr.$$

Similarly the mono-sodium derivative of the ester gives butane tetracarboxylic ester—

$$\begin{array}{l}CH_2Br + NaCH(COOC_2H_5)_2\\|\\CH_2Br + NaCH(COOC_2H_5)_2\end{array} = \underset{\text{Butane tetracarboxylic ester.}}{\begin{array}{l}CH_2{\cdot}CH(COOC_2H_5)_2\\|\\CH_2{\cdot}CH(COOC_2H_5)_2\end{array}} + 2NaBr.$$

The free acid, obtained by hydrolysis from butane tetracarboxylic ester, contains two pairs of carboxyl groups, each pair being linked to the same carbon atom, and consequently, on heating, two molecules of carbon dioxide are evolved. The resulting acid is a dibasic acid (adipic acid) of this series. In this way *the synthesis of dibasic acids* may be effected by the aid of malonic ester.

$$\underset{\text{Butane tetracarboxylic acid.}}{(COOH)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOH)_2} = \underset{\text{Adipic acid.}}{COOH{\cdot}(CH_2)_4COOH} + 2CO_2.$$

Succinic Acid, $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is mentioned by Agricola (1550) as being obtained from amber (Lat. *succinum*) by distillation, and the method is still used in its preparation. When amber is distilled in iron retorts, the acid collects in the receiver partly in

the solid form and partly in solution, together with an oil, known as *amber oil*. The distillate is then filtered from the oil and evaporated. Succinic acid occurs in certain lignites and fossil wood, and in lettuces, unripe grapes, and wormwood. It is also obtained by the fermentation of calcium malate or ammonium tartrate by yeast or putrid cheese. The process is one of reduction, and may be imitated by the action of strong hydriodic acid.

$$\begin{array}{l} CH(OH){\cdot}CO{\cdot}OH \\ | \\ CH(OH){\cdot}CO{\cdot}OH \end{array} \qquad \begin{array}{l} CH(OH){\cdot}CO{\cdot}OH \\ | \\ CH_2{\cdot}CO{\cdot}OH \end{array} \qquad \begin{array}{l} CH_2{\cdot}CO{\cdot}OH \\ | \\ CH_2{\cdot}CO{\cdot}OH \end{array}$$

Tartaric acid. Malic acid. Succinic acid.

When either tartaric or malic acid is heated with strong hydriodic acid, it is converted into succinic acid, just as glycollic acid under the same conditions forms acetic acid (p. 319). Succinic acid has also been synthesised by a method which leaves no doubt as to its constitution. When ethylene dibromide is boiled with potassium cyanide, ethylene cyanide is formed. The latter, on hydrolysis, gives succinic acid. As ethylene dibromide is prepared from ethylene and ethylene may be obtained from acetylene, which is formed by the direct union of carbon and hydrogen, succinic acid can be synthesised from its elements—

$$\begin{array}{l} CH \\ ||| \\ CH \end{array} \xrightarrow{H_2} \begin{array}{l} CH_2 \\ | \\ CH_2 \end{array} \xrightarrow{Br_2} \begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} \xrightarrow{KCN} \begin{array}{l} CH_2CN \\ | \\ CH_2CN \end{array} \xrightarrow{H_2O} \begin{array}{l} CH_2{\cdot}CO{\cdot}OH. \\ | \\ CH_2{\cdot}CO{\cdot}OH. \end{array}$$

Acetylene. Ethylene. Ethylene bromide. Ethylene cyanide. Succinic acid.

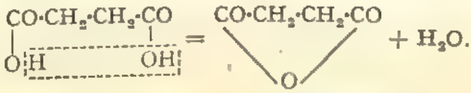
Succinic acid can also be obtained from β-iodopropionic acid by the action of potassium cyanide and by hydrolysing the resulting cyanopropionic acid. There are many other methods of preparation, which are of less importance—

$$\underset{\beta\text{-Iodopropionic acid.}}{ICH_2{\cdot}CH_2{\cdot}COOH} \longrightarrow \underset{\beta\text{-Cyanopropionic acid.}}{CN{\cdot}CH_2{\cdot}CH_2{\cdot}COOH}$$

$$\longrightarrow \underset{\text{Succinic acid.}}{COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH.}$$

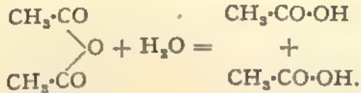
Succinic acid crystallises in prisms, or plates, which melt at 182°. When distilled it is converted into the anhydride, a white crystalline substance, which melts at 120°. The fact that succinic acid alone among the simple dibasic acids gives an anhydride is

explained on the same grounds as those which determine the formation of the lactones from the γ- and δ-hydroxy-acids (p. 320).

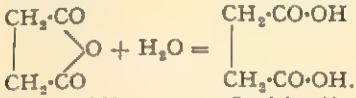


Succinic anhydride.

Succinic anhydride, like acetic anhydride, is converted into the acid by boiling with water or alkalis—

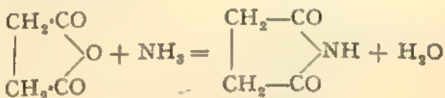


Acetic anhydride. Acetic acid.



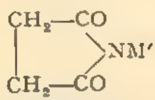
Succinic anhydride. Succinic acid.

When succinic anhydride is heated in a current of ammonia, succinimide is formed—



Succinimide.

Succinimide is a crystalline substance which has the properties of weak acid, inasmuch as the hydrogen of the NH group is replaceable by certain metals, and forms salts of the general formula—



General formula of Succinimide salts.

Succinic acid forms a series of well-defined salts, among which the calcium and basic ferric salts are characteristic. The latter is thrown down as a light brown, gelatinous precipitate on adding ferric chloride to a solution of a succinate. Iron may be separated from other metals by this means.

Isosuccinic Acid, *Methyl malonic acid,* $CH_3 \cdot CH(CO \cdot OH)_2$, is isomeric with succinic acid and is obtained from malonic ester by the action of methyl iodide on sodium malonic ester. The free acid loses carbon dioxide on heating, and yields propionic acid (p. 348).

Pyrotartaric Acid, *Methyl succinic acid,* $CH_3 \cdot CH(COOH) \cdot CH_2(COOH)$, is isomeric with glutaric acid and dimethyl malonic acid. It is obtained by the dry distillation of tartaric acid. Like succinic acid it forms an anhydride.

Adipic Acid, $CO \cdot OH(CH_2)_4CO \cdot OH$, was first obtained by the oxidation of fat (Lat. *adeps*). It has been synthesised by various methods; by the electrolysis of potassium ethyl succinate (p. 334); by the action of ethylene bromide on sodium malonic ester (p. 349); and by decomposing β-iodopropionic acid with finely divided metallic silver—

$$Ag_2 + \underset{\beta\text{-Iodopropionic acid.}}{\begin{matrix} ICH_2 \cdot CH_2 \cdot COOH \\ ICH_2 \cdot CH_2 \cdot COOH \end{matrix}} = 2AgI + \underset{\text{Adipic acid.}}{\begin{matrix} CH_2 \cdot CH_2 \cdot COOH \\ | \\ CH_2 \cdot CH_2 \cdot COOH \end{matrix}}$$

Hydroxy-dibasic Acids

Malic Acid, *Hydroxysuccinic acid,* $COOH \cdot CH(OH) \cdot CH_2 \cdot COOH$.—The acid was isolated by Scheele, in 1785, from the juice of unripe apples (Lat. *malum*), and it frequently accompanies tartaric and citric acid (see pp. 354, 359) in fruits, partly in the free state and partly as the potassium or calcium salt. In currants, cherries, and in the leaves and stems of rhubarb, it is present as the acid potassium salt; in the tobacco plant, as the acid calcium salt.

It is usually prepared from the unripe berries of the mountain ash. The juice is boiled with milk of lime which precipitates the neutral calcium salt, $C_4H_4O_5Ca$. The precipitate is collected and washed, and recrystallised from hot, dilute nitric acid, from which the acid salt separates, $(C_4H_5O_5)_2Ca + 6H_2O$. This is decomposed with the theoretical quantity of oxalic or sulphuric acid, and the liquid, filtered from the calcium oxalate or sulphate, is concentrated by evaporation. Malic acid is a crystalline substance which melts at about 100°. It is very hygroscopic, and deliquesces on exposure to moist air. When heated it loses water, and is converted into two isomeric acids, known as fumaric and maleic acids, which will be described later (p. 362)—

$$C_4H_6O_5 - H_2O = \underset{\text{Fumaric and Maleic acids.}}{C_4H_4O_4}.$$

The structure of malic acid has been determined in various ways. It is readily reduced by hydriodic acid to succinic acid, and is therefore a derivative of succinic acid. When monobromosuccinic acid is acted upon with moist silver oxide, it is converted into malic acid. It is therefore hydroxysuccinic acid—

$$\begin{array}{lcl} OH\boxed{Ag + Br}CH{\cdot}COOH & = & (OH)CH{\cdot}CO{\cdot}OH \\ \qquad\qquad\quad | & & \qquad\ \ | \qquad\qquad\qquad + AgBr \\ \qquad\qquad CH_2{\cdot}COOH & & \qquad CH_2{\cdot}COOH. \\ \text{Monobromosuccinic acid.} & & \text{Malic acid.} \end{array}$$

Moreover, hydrobromic acid yields monobromosuccinic acid; phosphorus chloride, monochlorosuccinic acid; and acetyl chloride, acetyl malic acid—

$$\begin{array}{l} C_2H_3O{\cdot}OCH{\cdot}CO{\cdot}OH \\ \qquad\qquad\ | \\ \qquad\quad\ CH_2{\cdot}CO{\cdot}OH. \\ \quad\ \text{Acetyl malic acid.} \end{array}$$

All these reactions give evidence of the presence of a hydroxyl group in the acid. The natural acid from berries is lævo-rotatory

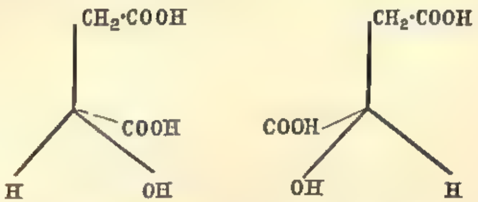


FIG. 83.—Space configuration of isomeric malic acids.

in dilute solution, which points to the existence of an asymmetric molecule. The corresponding dextro-rotatory acid is obtained by the partial reduction of ordinary tartaric acid (see p. 356) with hydriodic acid. The existence of these two acids receives the same explanation as that of the two lactic acids. The space configuration of the two isomers is represented in Fig. 83.

The synthetic malic acids obtained from bromosuccinic acid and by the reduction of inactive racemic acid (p. 358) are inactive, and consist of a mixture of equal quantities of the two active components. It is usual to find the artificial products of the laboratory, prepared from inactive materials, to be themselves inactive; and

this is readily understood when we consider that there is only a single property, the action on polarised light, which distinguishes the two components. Chemically they are identical, and therefore, in any chemical change, the formation of the one isomer necessitates, under ordinary conditions, the production of an equal quantity of the second.

Asparagine, *Aminosuccinamide*, $COOH{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO(NH_2)$, receives its name from having been first found in asparagus (1805); but it is very widely distributed in the vegetable kingdom, and is present in the parts of the plant which afford a store of reserve material, such as bulbs, tubers, and seedlings. The dried seedlings of lupines contain 20–30 per cent. of asparagine. It yields aspartic acid on hydrolysis with caustic potash solution—

$$\begin{array}{l} CH(NH_2){\cdot}COOH \\ | \\ CH_2{\cdot}CO|NH_2 \\ \quad\quad\;\; | \\ + H\ O|H \\ \text{Asparagine.} \end{array} = \begin{array}{l} CH(NH_2){\cdot}COOH \\ | \\ CH_2{\cdot}COOH. \\ \text{Aspartic acid.} \end{array} + NH_3$$

Aspartic Acid, *Aminosuccinic acid*, $COOH{\cdot}CH(NH_2){\cdot}CH_2{\cdot}COOH$, occurs in beet-root molasses, and is formed from albuminoid substances by the action of mineral acids. It is converted into malic acid by the action of nitrous acid. The reaction resembles the conversion of a primary amine into an alcohol, or of glycine into glycollic acid (p. 325).

Glutamic Acid, *Aminoglutaric acid*, $COOH{\cdot}CH(NH_2){\cdot}CH_2CH_2{\cdot}COOH$, frequently accompanies aspartic acid, and is chiefly interesting from its occurrence among the products of decomposition of albumin, formed by boiling with mineral acids.

Tartaric Acid, *Dihydroxysuccinic acid*,

$$COOH{\cdot}CH(OH){\cdot}CH(OH){\cdot}COOH.$$

Tartaric acid in the form of the acid potassium salt has been known since wine was made from grapes. It is deposited during fermentation as a brown, crystalline crust, known as *argol*, or wine-lees. The term tartar was given by the alchemists to both animal and vegetable concretions, and wine lees, stone, gravel, and the deposit on teeth, being attributed to the same cause, received the same name. Tartaric acid was isolated and recognised as a distinct acid by Scheele in 1769, who described it in his first scientific paper. As the free acid and as the acid potassium salt it

is widely distributed throughout the vegetable kingdom. It is found with malic acid in the berries of the mountain ash, and in other berries and fruits, but the chief source is grape juice. During fermentation the acid potassium salt in the juice is rendered insoluble by the alcohol, and gradually separates in minute crystals which carry down some of the colouring matter of the wine. The brown powder, or argol, is recrystallised for the production of the pure salt which is known as *cream of tartar*.

In order to prepare tartaric acid, the argol is dissolved in water, and chalk is added until the solution is nearly neutralised. The insoluble calcium tartrate, which is deposited, is separated by filtration from the neutral potassium tartrate which is in solution. A further quantity of calcium tartrate is obtained from the filtrate by adding calcium chloride. The process is represented by the following equations—

$$\underset{\text{Acid potassium tartrate.}}{2C_4H_5O_6K} + CaCO_3 = \underset{\text{Calcium tartrate.}}{C_4H_4O_6Ca} + \underset{\text{Potassium tartrate.}}{C_4H_4O_6K_2} + CO_2 + H_2O.$$

$$C_4H_4O_6K_2 + CaCl_2 = C_4H_4O_6Ca + 2KCl.$$

The calcium tartrate is then decomposed by the addition of sulphuric acid, and the solution, filtered from calcium sulphate, is concentrated and allowed to cool, when crystals of tartaric acid separate. The potassium chloride is recovered and used in the manufacture of potash salts.

Tartaric acid crystallises in large, transparent prisms, which dissolve in water and alcohol and melt at about 170° with decomposition. It is dextro-rotatory in aqueous solution. When heated by itself it forms pyrotartaric acid (p. 352); with potassium hydrogen sulphate, it yields pyruvic acid (p. 327).

Salts of Tartaric Acid.—Tartaric acid forms acid and neutral salts and salts with two different bases. The acid salts of potassium and ammonium are sparingly soluble in cold water.

EXPT. 129.—Add a little potassium nitrate, or acetate, solution and a few drops of dilute acetic acid to a strong solution of tartaric acid, and stir with a glass rod. The acid potassium salt of tartaric acid is precipitated. A similar precipitate of acid ammonium tartrate is formed when an ammonium salt is used in place of the potassium salt.

The normal salts of the alkalis are all readily soluble in water. *Rochelle salt*, or potassium sodium tartrate, $C_4H_4O_6KNa + 4H_2O$, so called after its discoverer, Seignette de la Rochelle, is prepared by neutralising a solution of cream of tartar with sodium carbonate solution. The solution is then evaporated, and deposits, on cooling, large transparent crystals. *Tartar emetic*, $C_4H_4O_6K(SbO) + \frac{1}{2}H_2O$, is prepared by dissolving antimonious oxide in a solution of cream of tartar. It crystallises in rhombic octahedra. It dissolves in water, and is used in medicine as an emetic and in cotton dyeing as a mordant (p. 445).

Detection of Tartaric Acid.—Tartaric acid is detected by the formation of the insoluble calcium salt, $C_4H_4O_6Ca + 4H_2O$, on the addition of calcium chloride to the neutral solution. The calcium salt is distinguished from calcium oxalate by its solubility in caustic alkalis and acetic acid. It may also be detected by Fenton's reagent (p. 52).

Expt. 130.—Dissolve a normal salt of tartaric acid in water. Add a drop of ferrous sulphate solution, a few drops of hydrogen peroxide solution, and make alkaline with caustic soda. A violet solution is obtained.

When tartaric acid or its salts are strongly heated they char and emit an odour of burnt sugar.

A further test is the reduction of silver tartrate in alkaline solution as follows :—

Expt. 131.—Dissolve some Rochelle salt or other neutral salt in water, and add a solution of silver nitrate. A white precipitate of silver tartrate is thrown down. Add dilute ammonia solution drop by drop until the precipitate nearly vanishes, and place the vessel in a beaker of hot water. A mirror of silver is deposited.

Structure of Tartaric Acid.—Tartaric acid is a dibasic acid and it forms alkyl esters—viscid liquids, which can be crystallised. Methyl tartrate is dimorphous, the two forms melting at 48° C. and 61·5° C. respectively, whilst ethyl tartrate melts at 18·7° C. These esters react with acid chlorides and form mono- and di-acyl esters; whilst strong nitric acid gives a dinitroxy-ester. Taken in conjunction with the fact that tartaric acid undergoes reduction to malic and succinic acids (p. 350), the formation of acyl esters

affords additional evidence of the acid being a dihydroxy-succinic acid—

$$\begin{array}{c|c|c}
\begin{array}{l} CH(OH)\cdot COOC_2H_5 \\ | \\ CH(OH)\cdot COOC_2H_5 \end{array} & \begin{array}{l} (C_2H_3O)\cdot OCH\cdot COOC_2H_5 \\ \qquad\qquad\quad | \\ (C_2H_3O)\cdot OCH\cdot COOC_2H_5 \end{array} & \begin{array}{l} (NO_2)O\cdot CH\cdot COOC_2H_5 \\ \qquad\quad\; | \\ (NO_2)O\cdot CH\cdot COOC_2H_5 \end{array} \\
\text{Diethyl tartrate.} & \text{Diacetyl tartaric ester.} & \text{Dinitroxy-tartaric ester.}
\end{array}$$

When heated with concentrated hydrobromic acid, tartaric acid yields dibromsuccinic acid, whereas hydriodic acid exerts a reducing action, giving first malic and finally succinic acid, thus—

$$\begin{array}{l} CH(OH)\cdot COOH \\ | \\ CH(OH)\cdot COOH \end{array} + 2HBr = \underset{\text{Dibromsuccinic acid.}}{\begin{array}{l} CHBr\cdot COOH \\ | \\ CHBr\cdot COOH \end{array}} + 2H_2O.$$

$$\begin{array}{l} CH(OH)\cdot COOH \\ | \\ CH(OH)\cdot COOH \end{array} + 2HI = \underset{\text{Malic acid.}}{\begin{array}{l} CH_2\cdot COOH \\ | \\ CH(OH)\cdot COOH \end{array}} + H_2O + I_2$$

$$\begin{array}{l} CH(OH)\cdot COOH \\ | \\ CH(OH)\cdot COOH \end{array} + 4HI = \begin{array}{l} CH_2\cdot COOH \\ | \\ CH_2\cdot COOH \end{array} + 2H_2O + 2I_2.$$

The existence of four hydroxyl groups in the molecule of tartaric acid is readily confirmed by the action upon it of acetic anhydride in the presence of a trace of concentrated sulphuric acid, which condenses the two carboxyl groups to an anhydride ring and at the same time acetylates the two alcoholic groups—

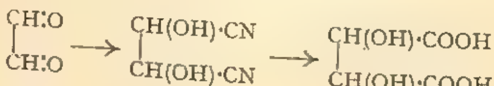
$$\begin{array}{l} CH(OH)\cdot COOH \\ | \\ CH(OH)\cdot COOH \end{array} + \begin{array}{l} CH_3\cdot CO \\ CH_3\cdot CO \end{array}\!\!>O = \underset{\text{Diacetyl tartaric anhydride.}}{\begin{array}{l} CH_3\cdot CO\cdot O\cdot CH\cdot CO \\ \qquad\qquad\quad | \\ CH_3\cdot CO\cdot O\cdot CH\cdot CO \end{array}\!\!>O} + 2H_2O.$$

EXPT. 131*a*.—Mix well together in a dry, round-bottomed flask 10 grams of well-powdered tartaric acid with about 25–30 grams of acetic anhydride. Then add not more than 5 drops of concentrated sulphuric acid. The mixture when shaken becomes warm and the tartaric acid dissolves gradually. Slight further heating may be necessary in order to obtain a clear solution. On cooling, crystals of diacetyl tartaric anhydride separate. Filter them off by suction, recrystallise them once from fresh acetic anhydride, wash them with dry ether until they are free from the smell of the solvent; they can then be recrystallised from benzene. When quite pure they melt at 134° C. They are strongly dextro-rotatory, $[\alpha]_D^{20°} = +61{\cdot}9°$.

Tartaric acid exists in four isomeric modifications, viz.—ordinary or *d*-tartaric acid, lævo-tartaric acid and two optically inactive forms, called racemic acid and meso-tartaric acid, respectively. Inspection of their formulæ shows that the optical activity is accounted for by the presence in the molecule of two asymmetric carbon atoms, and that each of them is combined with the same four groups. Thus the activity of one of them may be completely balanced by that of the other. This is called *internal compensation*, and is the cause of the optical inactivity of meso-tartaric acid. The stereoisomerism of the acid will be discussed more fully in Chapter XXIII.

Lævo-tartaric Acid, $C_4N_6O_6$.—Lævo-tartaric acid has been prepared from racemic acid by a method of resolution which will be described later. It resembles *d*-tartaric acid in all properties, other than crystalline form and the sign of its rotation.

Racemic Acid, $(C_4H_6O_6)_2 \cdot 2H_2O$.—Racemic acid has long been known as a by-product in the mother-liquors from cream of tartar, and in 1830 Berzelius showed that its chemical composition was identical with that of tartaric acid, but the properties of the two acids differ in important respects, and he introduced the term *isomerism* in connection with them, although several other cases of isomerism had been observed. The crystalline forms of the two acids are different, and also their melting points. Tartaric acid is anhydrous, racemic acid crystallises with water of crystallisation, and the former is considerably more soluble in water than the latter. Their salts show similar differences, and, most important of all, racemic acid and its salts are optically inactive, but they can be resolved into the two active tartrates. Racemic acid can be obtained from tartaric acid by heating the latter with water in a sealed tube to 175° C. or by boiling a solution of the acid with a strong solution of caustic soda, when rearrangement of the groups takes place. It has been synthesised from glyoxal by forming the dicyanhydrin and hydrolysing the product—



Glyoxal — Glyoxal cyanhydrin. — Racemic acid.

It should be noted that whenever attempts are made to synthesise an optically active substance from inactive compounds, the product is invariably inactive.

Meso-tartaric Acid, $C_4H_6O_6$.—Another stereoisomer of tartaric acid is formed, together with racemic acid, when tartaric acid is heated with caustic soda or with water in a sealed tube at 165° C. It is optically inactive, but cannot be resolved into active components. It has been obtained synthetically by the action of moist silver oxide on dibrom-succinic acid, a reaction from which its structure can be deduced.

$$Ag_2O + H_2O + \underset{\substack{\text{Dibromosuccinic} \\ \text{acid.}}}{\begin{array}{l} BrCH\cdot COOH \\ \quad | \\ BrCH\cdot COOH \end{array}} = \underset{\substack{\text{Mesotartaric} \\ \text{acid.}}}{\begin{array}{l} (HO)CH\cdot COOH \\ \qquad | \\ (HO)CH\cdot COOH \end{array}} + 2AgBr.$$

Mesotartaric acid crystallises in rectangular tables, with one molecule of water. It melts at 140° and is more soluble than racemic acid. The most characteristic salt of this acid is calcium mesotartrate, $C_4H_4O_6Ca + 3H_2O$, which is insoluble in acetic acid and much less soluble in water than ordinary calcium tartrate. It is optically inactive.

Citric Acid, $C_6H_8O_7 + H_2O$, is present as the free acid in lemon juice, and in the juice of oranges, limes, sloes, etc. It is found with malic acid in gooseberries, currants, and other fruits and with malic and tartaric acids in mountain-ash berries. It also occurs as the calcium and potassium salts in many plants. It is obtained from lemon juice, which contains 7–8 per cent. of the acid, by neutralising with chalk or lime, and boiling the liquid. The calcium salt, which is insoluble in hot water, is thrown down and filtered. It is then decomposed with sulphuric acid. On evaporating the filtrate from calcium sulphate, citric acid crystallises in large transparent crystals containing 1 molecule of water. Lemon juice which contains the acid, should not be confounded with oil of lemons, which is obtained from the rind, and contains substances belonging to the family of terpenes (p. 507).

Citric acid is now prepared on an industrial scale by the citric fermentation of glucose, whereby 50 per cent. of the glucose is converted into citric acid. The ferment is a fungus which breaks up the glucose into citric acid and carbon dioxide. Citric acid is a tribasic acid, and forms three series of salts. The potassium and

sodium salts of citric acid can be prepared containing 1, 2, and 3 atoms of the metal in place of hydrogen. The calcium salt, $(C_6H_5O_7)_2Ca_3 + 4H_2O$, is characteristic of the acid. It is not precipitated on adding lime-water to a cold solution of citric acid, or calcium chloride to a citrate; but on boiling, the calcium salt, which is less soluble in hot water than cold, is thrown down. In this way the acid may be distinguished from some of the other acids derived from vegetable sources.

Ferric ammonium citrate is prepared for medicinal purposes in thin transparent flakes, by evaporating a solution of ferric citrate in ammonia on glass plates, and breaking up the hard film which remains.

Structure of Citric Acid.—When citric acid is heated to 175°, it loses a molecule of water, and gives aconitic acid, an acid which is also found in aconite—

$$C_6H_8O_7 - H_2O = \underset{\text{Aconitic acid.}}{C_6H_6O_6}.$$

Aconitic acid is tribasic, and is unsaturated; for, by the action of sodium amalgam, it takes up 2 atoms of hydrogen, and forms tricarballylic acid, which is also tribasic—

$$C_6H_6O_6 + H_2 = \underset{\text{Tricarballylic acid.}}{C_6H_8O_6}.$$

Tricarballylic acid, being tribasic, contains 3 carboxyl groups. Each of these groups will probably be united to 3 different carbon atoms of a chain. This accounts for 6 carbon, 6 oxygen, and 3 hydrogen atoms. By distributing the remaining 5 hydrogen between the 3 carbon atoms of the chain, we arrive at the following formula for tricarballylic acid—

$$\begin{array}{l} CH_2{\cdot}COOH \\ | \\ CH{\cdot}COOH \quad \text{Tricarballylic acid.} \\ | \\ CH_2{\cdot}COOH. \end{array}$$

What is the relationship of tricarballylic acid to aconitic and citric acids? Aconitic acid contains 2 hydrogen atoms less than tricarballylic acid. It will probably have the formula—

$$\begin{array}{l} CH\cdot COOH \\ \| \\ C\cdot COOH \\ | \\ CH_2\cdot COOH. \end{array} \quad \text{Aconitic acid.}$$

The addition of the elements of a molecule of water to aconitic acid will offer a choice between the following formulæ for citric acid—

$$\begin{array}{l} CH(OH)\cdot CO\cdot OH \\ | \\ CH\cdot CO\cdot OH \\ | \\ CH_2\cdot CO\cdot OH \end{array} \qquad \begin{array}{l} CH_2\cdot COOH \\ | \\ C(OH)\cdot COOH \\ | \\ CH_2\cdot COOH. \end{array}$$

Probable formulæ of Citric acid.

The presence of a hydroxyl group, which is assumed in these formulæ, is confirmed by the formation of an acetyl derivative of citric acid by the action of acetyl chloride on the ethyl ester. The position of the hydroxyl group has been determined by synthesis.

Synthesis of Citric Acid.—Glycerol dichlorhydrin (p. 280), gives dichloracetone on oxidation. The latter forms a cyanhydrin with hydrocyanic acid, and the cyanhydrin yields a hydroxy-acid on hydrolysis. The two atoms of chlorine may now be replaced by cyanogen groups by the action of potassium cyanide on the potassium salt of the acid. The dicyano-derivative is then converted into citric acid by boiling with hydrochloric acid. The series of processes may be represented as follows :—

$$\underset{\text{Glycerol dichlorhydrin.}}{\begin{array}{l} CH_2Cl \\ | \\ CH(OH) \\ | \\ CH_2Cl \end{array}} \longrightarrow \underset{\text{Dichlor-acetone.}}{\begin{array}{l} CH_2Cl \\ | \\ CO \\ | \\ CH_2Cl \end{array}} \longrightarrow \underset{\text{Dichloracetone cyanhydrin.}}{\begin{array}{l} CH_2Cl \\ | \\ C(OH)CN \\ | \\ CH_2Cl \end{array}} \longrightarrow \underset{\text{Dichlor-}\alpha\text{-oxybutyric acid.}}{\begin{array}{l} CH_2Cl \\ | \\ C(OH)\cdot COOH \\ | \\ CH_2Cl \end{array}}$$

$$\longrightarrow \underset{\text{Dicyan-}\alpha\text{-oxybutyric acid.}}{\begin{array}{l} CH_2CN \\ | \\ C(OH)\cdot COOH \\ | \\ CH_2CN \end{array}} \longrightarrow \underset{\text{Citric acid.}}{\begin{array}{l} CH_2\cdot CO\cdot OH \\ | \\ C(OH)\cdot CO\cdot OH \\ | \\ CH_2\cdot CO\cdot OH \end{array}}$$

8. How is oxalic acid made on the large scale? What reactions occur between oxalic acid and (*a*) alcohol, (*b*) sulphuric acid, (*c*) phosphorus pentachloride?

9. What is the formula of oxalic acid? How is it made? How can ammonium oxalate be prepared? What is its relationship to cyanogen?

10. Starting from acetic acid, how would you prepare the diethyl ester of malonic acid, and how would you obtain acetic acid from the ester?

11. Give examples of the synthesis of various compounds from malonic ester.

12. An acid which contains only carbon, hydrogen, and oxygen gave on analysis 40·7 per cent. of carbon and 5·08 per cent. of hydrogen. The silver salt contained 65 per cent. of silver. The acid on heating evolved carbon dioxide, leaving a strongly acid liquid. What is the probable composition of the acid and of the product formed on heating, and how is the former most easily prepared?

13. What are the chief natural sources and chemical relationships of succinic, malic, and tartaric acids? How may these acids be changed into each other?

14. How many tartaric acids are known? How are they obtained? How do you account for their existence?

15. Starting from ethylene, show by what series of operations tartaric acid may be built up. In what respect does the acid so formed differ from tartaric acid obtained from grapes?

16. Tartaric acid contains six atoms of oxygen, but is only dibasic. In what forms does the oxygen exist in this acid, and how is such a question determined?

17. What is the common source and mode of manufacture of citric acid? How has it been synthetically prepared and its constitution determined?

18. Explain the isomerism of maleic and fumaric acids. By what means can they be changed into tartaric acids, and how are they related to the different modifications of the latter?

CHAPTER XXIII

STEREOCHEMISTRY

REFERENCE was made in Chapter VII to the use of spatial formulæ and the asymmetric carbon atom in order to account for the optical isomerism of one of the amyl alcohols. The adoption of the regular tetrahedron to represent the probable configuration of the quadrivalent carbon atom has led to many important developments in the theory of the structure of molecules. It is assumed that in a completely symmetrical molecule, such as those of methane or carbon tetrachloride, the four valencies of the carbon atom radiate from its centre through the four corners. The angle between each pair of valency bonds is therefore $109\frac{1}{2}°$, and one pair lies in a plane at right angles to that of the other pair. When two carbon atoms are combined by a single bond, the two tetrahedra will be joined corner to corner (Fig. 84), but when three atoms are linked in a chain, the lines joining their centres will also be inclined to one another at an angle of $109\frac{1}{2}°$, a value slightly in excess of that of a regular pentagon (108°). Thus the ends of an unbranched chain of 5 carbon atoms will nearly meet, while the ends of a 6-carbon chain will overlap. This means, according to Baeyer, that in each case the chain must be strained slightly if the ends are to be united to form a closed ring. According to Baeyer's strain theory, closed chains of 5 or 6 members are more stable than any others, a conclusion which agrees with experience. Again, since the valencies diverge at an angle, two valencies of one atom will not mutually satisfy two of another unless they are strained from their normal directions. Consequently the double bond of ethylene is easily opened to permit the formation of addition compounds and, moreover, it must be a weaker link than that of ethane. It is well known that in a long-chained olefine a double bond is the first point of attack by reagents. The double bond involves the union of 2 tetrahedra *edge to edge*, while the triple bond of acetylene is represented by placing the 2 models *face to face* (Fig. 84). It is obvious that quadruple links are impossible.

The student is strongly recommended to construct a few simple models. Regular tetrahedra are easily and rapidly constructed from thin cardboard and gummed paper. Coloured paper gummed to the corners can represent other elements or groups. Two

tetrahedra may then be held together point to point to represent a single bond, edge to edge to represent a double bond, and face to face to represent a triple bond. No difficulty will then be encountered in understanding the following description of stereochemistry.

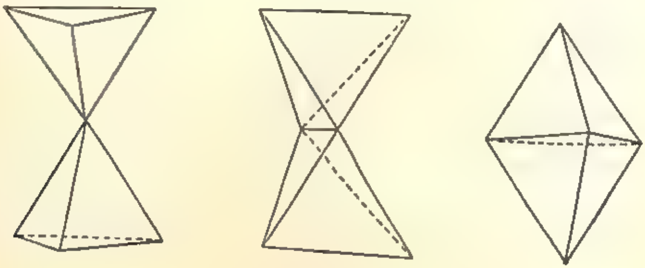


FIG. 84.

Geometric Isomerism.—Although any kind of stereoisomerism is geometric, the term *geometric isomerism* was devised by van 't Hoff, and is still used to denote a form of isomerism which is rather different from optical isomerism, though related to it. It will be seen from the models that the four hydrogen atoms of ethylene all lie in one plane. On the other hand, the nature of the double bond precludes the possibility of any rotation of the carbon atoms about their junction. The introduction of two substituents into the molecule will then give rise to a type of isomerism which is not possible in methane. In this way we can account for the isomerism of maleic and fumaric acids (p. 362). From their properties it is obvious that the two carboxylic groups are nearer together in the one which gives an anhydride (maleic acid) than in fumaric acid. Consequently we assign to maleic acid the structure in which both carboxyl groups are on the same side of the plane of the double bond (Fig. 85). The two forms are called the *cis*- (for maleic acid) and the *trans*-forms. The term geometric isomerism is used to denote any variety of *cis–trans* isomerism, which is due to a restriction of free rotation imposed by a double bond or its equivalent. Thus the closed ring of the hexahydrophthalic acids (p. 479) produces geometric isomerism. The double bond between the carbon and nitrogen atoms in certain of the aldoximes (p. 131) also gives rise to a type of geometric isomerism, but as

the groups involved in the isomerism in this case do not all lie in one plane, the prefixes *syn*- and *anti*- are used instead of *cis*- and *trans*-.

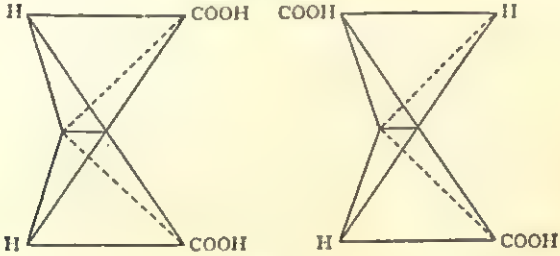


FIG. 85.

Projection Formulæ.—Although the models give the clearest and most accurate representation of the spatial distribution of groups, it is convenient to have a simpler method for ordinary use. Accordingly projections of these models are used so that a solid model can be conventionally represented in two dimensions, thus—

$\begin{array}{l} COOH\cdot C\cdot H \\ \qquad\quad \| \\ \qquad H\cdot C\cdot COOH \end{array}$	$\begin{array}{l} H\cdot C\cdot COOH \\ \quad\ \| \\ H\cdot C\cdot COOH \end{array}$	$\begin{array}{l} COOH\cdot C\cdot CH_3 \\ \qquad\quad \| \\ \qquad H\cdot C\cdot COOH \end{array}$	$\begin{array}{l} CH_3\cdot C\cdot COOH \\ \qquad\ \| \\ \quad H\cdot C\cdot COOH \end{array}$
Fumaric acid.	Maleic acid.	Mesaconic acid.	Citraconic acid.

It should be noted that geometric isomerism, although determined by space arrangement, is not characterised by optical activity, since no structural dissymmetry (p. 368) is possible. On the other hand, the *cis–trans* isomers, unlike optical isomers, differ from one another in physical properties, such as solubility, melting point, electrical conductivity, and by the fact that in the case of dibasic acids only one of the pair yields an anhydride. The isomerism of crotonic and isocrotonic acids (p. 271) and of oleic and elaidic acids (p. 272) is explained in the same manner.

Optical Isomerism.—Although optical isomerism is also spatial in character, the term "geometric" is not usually applied to it. The remarkable development in the theory of chemical structure, which followed its discovery, is rapidly being extended to inorganic compounds. Optical activity is accompanied by certain distinguishing features. Thus for every optically active substance there exists a twin form possessing exactly the same properties, except only as regards crystalline form and the sign of its optical

rotatory power. Moreover, the crystalline forms, though not identical, are related to one another as an object is related to its own reflection in a plane mirror. It is clear that a plane formula is not likely to give an adequate representation of the distribution of groups attached to a multivalent element like carbon. Nevertheless the necessity for adopting solid formulæ was not realised until the relation between optical activity and molecular structure was investigated by Pasteur in 1850, and satisfactorily interpreted in 1874 by Le Bel and van 't Hoff. The tetrahedral configuration of the carbon atom is now universally accepted, and the success which has followed its adoption has led to the use of other regular solid models, particularly the regular octahedron, for the interpretation of the structures of complex inorganic compounds.

Since organic compounds which are optically active exhibit this property in the liquid condition and even retain it in dilute solutions, Pasteur realised that it must be a property of the molecule. Quartz, on the other hand, loses its activity when its crystalline form is destroyed. Having shown that the twin crystalline forms of quartz have neither centres nor planes of symmetry, Pasteur associated their optical activity with this *dissymmetry* or lack of symmetry. In an attempt to account for the lack of rotatory power in racemic acid and its salts, which were chemically indistinguishable from tartaric acid and its salts, he discovered that crystals of the tartrates possess characteristic facets which render them dissymmetric, whereas racemic acid and racemates (with one important exception) possess no such facets. Pasteur defined a dissymmetric crystal as one which is not identical in form with its own mirror image. Crystals of sodium ammonium racemate do, however, possess facets, and are of two kinds. By a tedious process Pasteur separated the crystals into two varieties by picking them out from under a microscope. The two kinds were found to possess the characteristic features of dissymmetry (Fig. 86), and moreover when separately dissolved in water they were found to be dextro- and lævo-rotatory respectively.

Hence it was proved that the inactivity of the racemate was due to the presence of equal amounts of the two active forms, either mixed together or in combination. As already stated (p. 115), Le Bel and van 't Hoff attributed the optical activity of

The molecule of tartaric acid contains two such atoms, and can therefore be optically active. It must not be supposed, however, that the presence of an asymmetric atom in the molecule is necessary for the production of optical activity, for many optically active compounds are now known which possess none. But even in such cases the *whole molecule* is dissymmetric, and it is necessary to stress the point that *optical activity is caused by the dissymmetry either of the crystal or of the whole molecular structure rather than by the presence in the molecule of a particular grouping.* The terms "asymmetry" and "dissymmetry" are not identical, since the former signifies complete lack of symmetry, whereas the dissymmetric crystals of quartz, though devoid of any *plane* or *centre* of symmetry, still possess *axes* of symmetry. Another term for

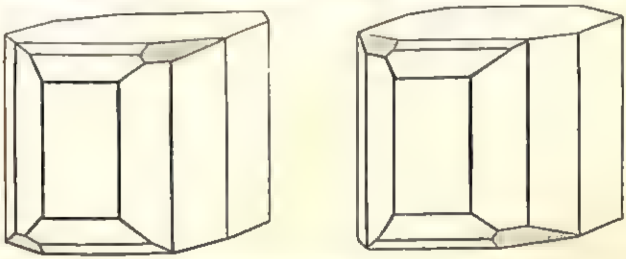


FIG. 86.—Enantiomorphous crystal forms of sodium ammonium tartrate.

dissymmetry is *enantiomorphism* (ἐναντίος, face to face; μορφή, form). The rotations of a pair of enantiomorphs are equal in magnitude but opposite in sign.

Nomenclature and Structure of the Tartaric Acids.—In order to distinguish between the active and inactive forms of tartaric acid and its salts, the two active forms are given the prefixes *d*- and *l*- respectively, whilst racemic acid is called *dl*-tartaric acid, since it can be resolved into the two active forms. Whenever optical inactivity is due to the simultaneous occurrence of enantiomorphs in equal amounts, whether mixed or combined, the compound is said to be *externally compensated,* and is called the *racemic* form, although the term racemic (Lat. *racemus,* a bunch of grapes) was originally used for *dl*-tartaric acid. There is, however, another inactive isomer of tartaric acid, which cannot be resolved into active components. It is called *meso-tartaric acid* or i-*tartaric*

halves of the molecule are dextro- and lævo-rotatory respectively. A glance at the structural formula of tartaric acid will show that each of the two asymmetric carbon atoms is combined with the same set of groups. Hence each half can be dextrorotatory or lævorotatory, thus giving the two active forms. Again, one form

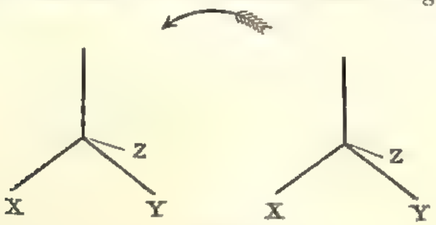
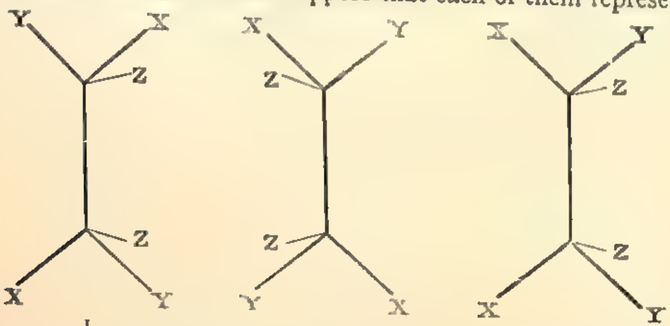


FIG. 87.

may be dextro- and the other lævo-rotatory, when the meso-form results. The explanation can be followed by reference to Figs. 87 and 87A. In Fig. 87, *X*, *Y*, and *Z* represent three different groups and the lines represent bonds radiating from the centres of the tetrahedra through the four corners. The two structures in Fig. 87 are identical. Let us suppose that each of them represents



I. Dextro-tartaric acid. II. Lævo-tartaric acid. III. Meso-tartaric acid.

Racemic acid.

FIG. 87A.

a *d*-compound. Then by inverting one of them and combining it with the other we obtain the model for *d*-tartaric acid (Fig. 87A I), and the *l*-acid will have the structure shown in Fig. 87A II. It is not possible as yet to determine with certainty which is dextro- and which is lævo-rotatory, so that an arbitrary choice has to be made. Fig. 87A III will then represent *i*-tartaric acid, as it is a

combination of the two forms. A convenient way of checking the result is to copy the lower halves of each of the models of Fig. 87A I and II on separate pieces of paper and then to rotate one of them *in the plane of the paper* and bring it over the other. Two-dimensional formulæ are apt to cause a considerable amount of confusion at first, and the student is very strongly urged to make paper models. When using the models it will be noticed that the

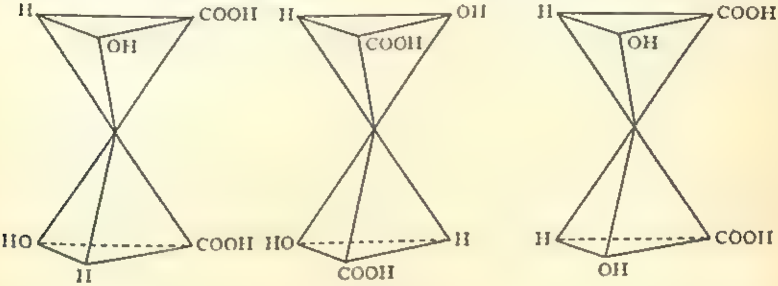
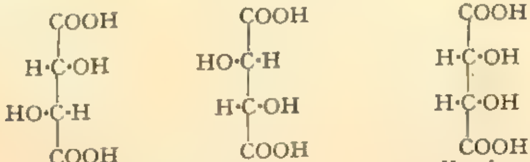


FIG. 87B.

two tetrahedra may be rotated about their common axis, and that in the case of an optically active form *only one group at a time* can be brought into position immediately above the same group in the other half; but in the case of the meso-compound there is one position in which all three groups will correspond with their opposite numbers. Although this fact is very helpful in forming a mental impression of the different configurations, there are reasons for believing that the carbon atoms are not really free to rotate, but have to take up positions of equilibrium.

Projection Formulæ.—As in the case of geometrical isomerism, we can conveniently adopt projection formulæ to represent optical isomers.



Optically active forms. Meso form.

Optical inactivity of the meso type is only possible, of course, when the molecule can be *halved*. Replacement of one hydroxyl group only by a chlorine atom would lead to the formation of an active meso form, since exact internal compensation would no

longer be possible. Again, every additional asymmetric atom introduced into the molecule produces a rapidly increasing number of possible stereoisomers. Sorbitol, dulcitol, and mannitol (p. 284) each contain 4 asymmetric atoms in the molecule, and represent 3 of 10 possible stereoisomers, all of which are known, 8 being active and 2 internally compensated. Corresponding with these are the ten saccharic acids (p. 291). When, on the other hand, the two terminal groups are different, as in glucose, internal compensation is impossible, and the number of isomers rises to 16, all of them optically active and all of them known. Of these glucose, mannose and galactose are the most important (pp. 289–300).

The Resolution of Externally-Compensated Compounds.—The principal methods for resolving inactive substances into their active components are due to Pasteur. The separation by the aid of the enantiomorphous crystalline forms of the salts has already been explained in the case of racemic acid; but the method is limited in its application by the fact that well-defined crystals which exhibit hemihedral facets cannot always be obtained. A more serviceable method is to combine the inactive substance, which is to be resolved, with an optically active compound; if a base, with an active acid; or, if an acid, with an active base. For supposing *d*A and *l*A stand for the dextro- and lævo- acids of racemic acid, the addition of an active (*e.g.* lævo) base B will produce a mixture of two different salts, *d*A*l*B and *l*A*l*B. The solubilities of the salts of dextro- and lævo-tartaric acid with the same active base, such as brucine (p. 587) are not the same, and the salts can be separated by fractional crystallisation. For resolving racemic acid, the racemate of an active base is prepared, and the salt crystallised. The least soluble portion, which first crystallises, is the salt of the one acid, and the more soluble that of the other. This process has been applied successfully to the resolution of inactive lactic acid, and to many other cases. A third method, also employed by Pasteur, is to cause a solution of the inactive substance to ferment, by introducing certain low vegetable organisms, such as yeast, moulds, or bacteria; one of the two active forms is, as a rule, more easily assimilated than the other, and the liquid shows increasing optical activity as the fermentation proceeds. Synthetic fructose, like other laboratory products obtained from inactive materials, is inactive; but, when fermented

with yeast, the natural fructose is assimilated whilst the dextro-rotatory sugar remains. In this way a dextro-rotatory fructose has been prepared.

Specific and Molecular Rotations.—Since the observed rotation of an optically active substance depends not only on the actual amount of active material in the observation tube but also on other factors, such as temperature and wave-length of light, it is necessary to adopt some ready means of recording the results in such a manner that the values can be checked and compared. It is advisable to record all readings at constant temperature. The rotation of a substance varies directly as the length of the observation column, the decimetre being used as unit of length. Thus the rotation of a 2-dcm. column will be twice that of a 1-dcm. column. One might expect, therefore, to find that the rotations would be directly proportional to the concentration in solution. This is by no means always the case; hence it is usual to record the actual concentration used. The specific rotation is an arbitrary value, calculated on the assumption that the rotation is always proportional to the concentration and is the value calculated for a 100 per cent. solution—*i.e.*, for a solution containing 100 grams of active material in 100 c.c. of solution and for a column 1 decimetre in length. It is represented by the symbol $[\alpha]_D^{20^\circ}$ for sodium light; otherwise the wave-length is added.

If the solution contains c grams of substance in 100 c.c. of solution and the length of the tube is l decimetres, then if α is the recorded reading

$$[\alpha]_D^{20^\circ} = \frac{\alpha \times 100}{c \times l};$$

but if the solution is made up by weight and contains p grams in 100 *grams* of solution, the density must be taken into account, and if d is the density

$$[\alpha]_D^{20^\circ} = \frac{\alpha \times 100}{p \times d \times l}.$$

For pure liquids, such as esters, it is also necessary to use the density. Sometimes it is more convenient to take the molecular weight into consideration. The molecular rotation is found by multiplying the specific rotation by the molecular weight and dividing by 100, in order to avoid high values.

$$[M]_D^{20^\circ} = \frac{[\alpha]_D^{20^\circ} \times \text{Mol. wt.}}{100}.$$

Racemisation.—It frequently happens that optically active compounds become inactive by external compensation when heated with water or other reagent. This appears to involve a form of tautomerism, but the mechanism of the reaction is not yet clearly understood. It is called racemisation.

Walden Inversion.—Another curious change which is still the subject of close investigation was first discovered by Walden in 1896. When *l*-chlorosuccinic acid reacts with moist silver oxide, replacement of the chlorine atom by the hydroxyl group results in the production of *l*-malic acid, whereas when potassium hydroxide is used instead of silver oxide the product is *d*-malic acid. Again, when *d*- and *l*-malic acids react with phosphorus pentachloride, the resulting chlorosuccinic acids are lævo- and dextro-rotatory respectively. Accordingly it is not possible to predict with certainty the sign of rotation of any product derived from an optically active compound by chemical substitution of one group for another.

Asymmetric Synthesis.—It has already been stated (p. 372) that whenever a substance with a dissymmetric structure is synthesised artificially from optically inactive substances, the product is invariably inactive by external compensation, since the *d*- and *l*-forms differ from one another only in crystalline form and in the sign of their rotatory power. Since, however, optically active compounds are commonly produced in living processes, many attempts have been made to effect the direct synthesis of an active substance. Nearly all the cases hitherto recorded have, however, involved the use of an active reagent. This may also happen in the living cells, but the problem of the *original* separation of optical isomerides remains unsolved. Some interesting results have, however, been obtained which involve photodecompositions by ultra-violet light, but the subject cannot be discussed here.

Other Types of Optical Activity.—1. Optical activity may be due to the presence in the molecule of asymmetric atoms of quadrivalent sulphur, selenium, silicon, and tin, as well as of quinquevalent nitrogen and phosphorus. In the case of quinquevalent elements the regular tetrahedron is still used as the model, since it is known that only four of the valencies are co-valencies (p. 378), the fifth being an electrovalence. An interesting variation has been discovered in some of the compounds of phosphorus, in which a double bond was found to consist of one co-valent and one electro-

valent link. This is called a semi-polar double bond (Chapter XXIV).

2. Dissymmetric molecules which contain no asymmetric atoms are also known. We have seen that the four hydrogen atoms in ethylene all lie in one plane. If three carbon atoms were to be linked in a chain by *two* double bonds, thus, C⁚C⁚C, the four valencies at the ends would lie in two planes, as in the case of methane. The structure of the hydrocarbon allene, $H_2C{:}C{:}CH_2$, would then be that of an irregular tetrahedron. The compound diphenyl-dinaphthylallene—

$$\begin{array}{l} C_6H_5 \\ C_{10}H_7 \end{array}\!\!>C{:}C{:}C<\!\!\begin{array}{l} C_6H_5 \\ C_{10}H_7 \end{array}$$

has been made by Maitland and Mills and resolved into its optical isomers.

It will be noticed that in this case the four groups attached to the irregular tetrahedron are not all different. A somewhat similar compound was resolved in 1909 by Perkin, Pope and Wallach. In it one of the two double bonds was replaced by a closed-ring structure, which gives much the same effect. The compound was 1-methyl cyclohexylidene 4-acetic acid—

$$\begin{array}{l} CH_3 \\ H \end{array}\!\!>C<\!\!\begin{array}{l} CH_2{\cdot}CH_2 \\ CH_2{\cdot}CH_2 \end{array}\!\!>C{:}C<\!\!\begin{array}{l} H \\ COOH \end{array}$$

Several other types of optically active compounds have also been discovered, among them being derivatives of diphenyl (p. 514) which owe their dissymmetry to the restriction imposed on the free rotation of the two phenyl groups about their point of union by the presence of groups at certain positions which offer steric hindrance (p. 489). Another remarkable instance of optical activity is that of the cyclic polyhydric alcohol, *inositol* (p. 470), which is isomeric with glucose, but quite different from the carbohydrates in structure. The symmetry of its grouping—

$$CHOH<\!\!\begin{array}{l} CHOH{\cdot}CHOH \\ CHOH{\cdot}CHOH \end{array}\!\!>CHOH$$

shows that no asymmetric atom is present. Owing to the planar structure of the ring, no fewer than nine different groupings are possible, two of which form an enantiomorphous pair. One of the latter must represent natural inositol.

CHAPTER XXIV

THE ELECTRONIC THEORY OF VALENCY

At the end of the nineteenth century chemical valency meant little more than the ratio of atomic to equivalent weight, and although great success had been achieved in building up a satisfactory system of *molecular* structure in 3 dimensions, based on the quadrivalency of the carbon atom, no explanation was forthcoming of the essential difference in the structures of electrolytes and non-electrolytes, although the existence of positive and negative valencies was recognised. The study of *atomic* structures by Sir J. J. Thomson, Lord Rutherford, Bohr, and others opened the way to a clearer conception of the meaning of chemical valency. Moreover, since it is now recognised that all types of chemical combination are electrical in origin, increasing attention is being paid to the electronic interpretation of organic reactions, which have hitherto been imperfectly understood and apparently regulated by empirical rules, as in the case of addition reactions to unsaturated compounds or the substitution of aromatic hydrocarbons. A discussion of such problems is beyond the scope of this book, but electronic formulæ are so frequently used now that a brief description of them seems desirable.

Moseley's outstanding work with cathode rays (1913) revealed the existence of a definite sequence of atoms, which is not based on atomic weights, but on something more fundamental. This led to the idea that all atoms are derived from positively charged protons and negatively charged electrons in equal numbers, and that every atom consists of a positively charged nucleus surrounded by sufficient electrons to balance the charge. This nuclear charge is identical with Moseley's atomic number, and since the number of protons is equal to the atomic weight, it follows that the nucleus of hydrogen is a bare proton, that of helium consists of 4 protons and 2 electrons, that of lithium of 7 protons and 4 electrons, and so on, the difference between the number of protons and that of

electrons being the atomic number in each case. We need not consider the fusion of protons and electrons to neutrons, since only the outer skin of the atom is involved in the reactions with which we are concerned. Now, the extra-nuclear electrons must also be numerically equal to the atomic number, and it is believed that they are arranged in successive layers, of which the first can contain not more than 2 and the next two layers 8 each. Beyond that point complications arise, but the elements concerned are not often encountered in organic chemistry. The following table shows the distribution of extra-nuclear electrons :—

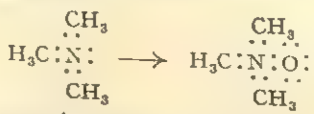
Element.	Atomic No.	Extra-nuclear electrons.		
		1st shell.	2nd shell.	3rd shell.
H	1	1	—	—
He	2	2	0	—
Li	3	2	1	—
Be	4	2	2	—
B	5	2	3	—
C	6	2	4	—
N	7	2	5	—
O	8	2	6	—
F	9	2	7	—
Ne	10	2	8	0
Na	11	2	8	1
Mg	12	2	8	2
Al	13	2	8	3
Si	14	2	8	4
P	15	2	8	5
S	16	2	8	6
Cl	17	2	8	7
A	18	2	8	8

The electronic theory of valency is based on the assumption that the most stable structures are those of the noble gases, neon, argon, etc., and that other atoms can assume the same structures by losing or gaining electrons, thus becoming charged or ionised. Thus sodium and magnesium lose 1 and 2 electrons respectively to acquire the structure of neon, forming Na^+ and Mg^{++} ions, whereas sulphur and chlorine have to gain electrons to acquire the structure of argon and form the ions S^{--} and Cl^-. Thus each *ion* has its full complement of electrons in the outer shell for stability, and the ions are held together in pairs by electrostatic attraction and not by

any material bond. This constitutes *electrovalency*, and is in harmony with the modern theory of complete ionisation, even in the solid condition, and is also supported by X-ray crystallographic analysis.

As one moves towards the centre of each period of elements, the power of gaining or losing electrons falls off very rapidly, so that when we reach carbon, ionisation seems to be inhibited. Instead of gaining or losing 4 electrons, carbon acquires stability by sharing electrons with other elements. This gives rise to a different type of compound, in which elements are combined by actual bonds, each of which consists of a pair of electrons. This type of valency is called *co-valency*, and is found not only in carbon compounds, but in all substances which form molecules—*e.g.*, water, ammonia, etc.

If we represent electrons by dots, the symbols for hydrogen, oxygen, and carbon atoms are $\mathrm{H}\cdot$, $:\!\ddot{\mathrm{O}}\!:$, and $:\!\mathrm{C}\!:$. The formula of water is then $\mathrm{H}\!:\!\underset{\cdot\cdot}{\ddot{\mathrm{O}}}\!:\!\mathrm{H}$, and that of carbon dioxide is $\underset{\cdot\cdot}{\ddot{\mathrm{O}}}\!::\!\mathrm{C}\!::\!\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$. It will be seen that each hydrogen atom has now its full quota of 2 electrons and the other atoms each have 8. This has been made possible by a process of sharing. It should be noticed that the two electrons which constitute a single bond are in each case contributed by different atoms. Some of the electrons of the oxygen atoms in the examples given are not shared by other atoms, and are called lone pairs. Lone pairs occur in other multivalent elements also, and it is found that these can sometimes be used to form compounds of still another type, called co-ordination compounds. The difference between a co-valent link and a co-ordinate link is that in the latter case both electrons of the pair are derived from the same atom. Thus the nitrogen atom in trimethylamine has a lone pair, which it can use to complete the octet of an oxygen atom to form trimethylamine oxide—



Similarly the oxygen in water can co-ordinate its lone pairs to other atoms, as in crystals containing water of crystallisation, and as in the Grignard reagents. A further type of valency which has often been identified with the co-ordination bond is known as a

semi-polar double bond. The double bond between the two carbon atoms in ethylene is a double co-valency, but the bond between phosphorus and oxygen in phosphoryl chloride is made up of one co-valency and one electrovalency, and is indicated by one of the following formulæ $\mathrm{Cl_3P \stackrel{\rightarrow}{=} O}$ or $\mathrm{Cl_3\overset{+}{P}-\overset{-}{O}}$. Phosphorus has 5 electrons. When 3 chlorine atoms are combined with it covalently, its octet is complete and there is one lone pair of electrons. If these were to be used with those of oxygen to form a co-valent double link, the phosphorus would have 10 electrons instead of 8. Instead of this it shares one electron and *donates* the other to the oxygen atom, thus forming a semi-polar double bond. The existence of such a bond has been confirmed by evidence derived from determinations of the parachor (a function of surface tension) and by the discovery of a new kind of optical activity. It should be noted that whereas electronic transference is involved in both polar (electrovalent) and non-polar (co-valent) compounds, the structures are quite different, and the real bond which is a feature of the latter is responsible for the existence of stereoisomerism. Investigation has shown that polar and non-polar combinations are to some extent interchangeable. Thus a non-polar bond may under favourable conditions break into two oppositely charged ions, thus facilitating chemical action. For example, when chlorine reacts with methane, the co-valent molecule of chlorine breaks unsymmetrically into oppositely-charged ions, thus

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow :\overset{-}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}}: \text{ and } \overset{+}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}}:$$

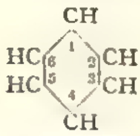
Similarly methane splits into negatively charged methyl and a hydrogen ion

$$\begin{array}{c}\mathrm{H}\\ \cdot\cdot\\ \mathrm{H}:\mathrm{C}:\mathrm{H}\\ \cdot\cdot\\ \mathrm{H}\end{array} \longrightarrow \begin{array}{c}\overset{-}{\mathrm{H}}\\ \cdot\cdot\\ \mathrm{H}:\mathrm{C}:\\ \cdot\cdot\\ \mathrm{H}\end{array} + \overset{+}{\mathrm{H}}$$

The positive and negative charges of the products are then neutralised by mutual interchange to give molecules of methyl chloride and hydrogen chloride.

$$\begin{array}{c}\mathrm{H}\\ \cdot\cdot\\ \mathrm{H}:\mathrm{C}:\mathrm{Cl}:\\ \cdot\cdot\\ \mathrm{H}\end{array} \text{ and } \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

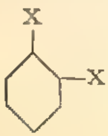
neither of which is ionised.



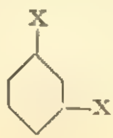
The existence of such a closed system of atoms presents nothing unusual, when we consider the structure of lactones (p. 320) and anhydrides of dibasic acids (p. 351) from a stereo-chemical point of view, as previously explained. This arrangement furnishes an explanation of many well-known properties of benzene. It explains its unusual stability towards reagents. It accounts for the existence of only one mono-derivative of benzene (that is, a derivative obtained by replacing one of the hydrogen atoms by another element or group); for the hydrogen atoms being symmetrically distributed, the 6 positions are identical. It explains, moreover, the occurrence of three isomeric di-derivatives. Isomeric di-derivatives of benzene are very common, but the maximum number is always three. There are three dichlorobenzenes, $C_6H_4Cl_2$, three dibromobenzenes, $C_6H_4Br_2$, three dinitrobenzenes, $C_6H_4(NO_2)_2$, etc.

Suppose we number the carbon atoms of the benzene ring from 1 up to 6, and represent the two new elements or groups by X. They can take up positions 1, 2; 1, 3; 1, 4; 1, 5, and 1, 6.

It is clear, however, that positions 1, 2 and 1, 3 are identical with 1, 6 and 1, 5. Three positions, therefore, remain, which will be those of the three isomers referred to above. These positions are known as *ortho-*, *meta-*, and *para*-positions.[1]



Ortho-

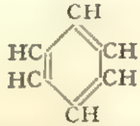


Meta-

Para-

[1] The names *ortho, meta,* and *para* will be occasionally indicated by the initial letters *o-, m-, p-* before the name of the substance. The numbers will also be used to denote the relative positions of atoms, or groups, in the ring.

It will be seen from the above formula for benzene that only three bonds of each carbon atom are appropriated. What is the function of the fourth carbon bond? In spite of many attempts to solve this problem, no completely satisfactory solution has yet been found, as one may judge from the constant use today of the convenient but unsatisfying formula put forward in 1865 by Kekulé. In Kekulé's original formula the carbon bonds were linked alternately by double and single bonds—



Kekulé's formula for Benzene.

This formula represents an unsaturated hydrocarbon of the olefine family (p. 246). Benzene is in fact very unlike the olefines, although it does form additive compounds with hydrogen, chlorine, and bromine, which have the properties of fully saturated compounds, but it does not combine with hydrogen chloride or hydrogen bromide—

C_6H_{12}	$C_6H_6Cl_6$	$C_6H_6Br_6$
Hexahydro-benzene.	Benzene hexachloride.	Benzene hexabromide.

The isomeric compound *dipropargyl*, which has already been described (p. 264), offers a great contrast to benzene in chemical properties, in so far as it requires 8 univalent atoms for saturation, yielding a parallel series of additive products with the following formulæ—

C_6H_{14}	$C_6H_6Cl_8$	$C_6H_6Br_8$
Hexane.	Octachloro-hexane.	Octabromo-hexane.

Moreover, dipropargyl is very sensitive to oxidising agents whereas benzene is marked by great stability.

The presence in the molecule of benzene of olefinic bonds is indicated in some of its reactions. Its oxidation by oxygen in the presence of vanadium pentoxide to maleic acid (p. 362) points to the existence of at least one double bond, and the fact that complete saturation is effected by the addition of 6 univalent atoms suggests the presence of 3 double bonds in a closed ring. The most remarkable confirmation of this is the formation of a

tri-ozonide, $C_6H_6(O_3)_3$, ozone being a well-known reagent for the detection and location of olefinic bonds.

On the other hand, Kekulé's formula for benzene fails to account for some of the characteristic properties of the olefines, which possess double linkages. Benzene and its derivatives form no additive compounds with the halogen acids, or strong sulphuric acid; nor are they, as a rule, oxidised by a solution of potassium permanganate in the cold, which rapidly attacks the olefines and their derivatives. Furthermore, the positions 1, 2 and 1, 6 are not strictly identical, for a double link is interposed between one pair of carbon atoms and a single link between the other pair—

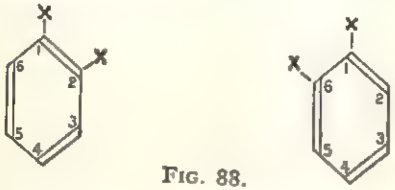
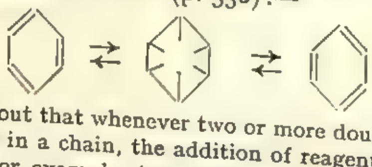


FIG. 88.

Consequently, 4 and not 3 di-derivatives should exist, and no example of the kind is known.

Kekulé's formula has therefore met with some opposition. The fate of the fourth carbon bond has been a long-debated problem.

Kekulé's own suggestion was that the double and single links might repeatedly change places, and if the oscillations were frequent enough, no difference between the two forms would be detected. Armstrong devised a *centric* formula, with all the fourth valencies directed to the centre, in order to account for the marked stability of the molecule. This formula was supported by experimental evidence by Baeyer, and it may be regarded as an intermediate phase in the oscillations of the Kekulé system, which is an example of dynamic isomerism (p. 330):—



Thiele pointed out that whenever two or more double bonds *alternate* with single bonds in a chain, the addition of reagents takes place in a peculiar way. For example, two hydrogen or halogen atoms would attack the extreme ends of the so-called *conjugated system of double bonds*, thus causing a complete rearrangement of bonds, instead of merely satisfying one of them, thus—

—CH:CH·CH:CH·CH:CH— ⟶ —CHBr·CH:CH·CH:CH·CHBr—

The chain therefore seems to exhibit a certain polarity which disappears as soon as the ends are joined to form benzene.

It may be pointed out that Kekulé's formula gives an *irregular* hexagon when constructed from regular tetrahedra, whereas crystallographic evidence points to the existence of a regular plane hexagon. On the other hand, the centric formula is not well suited for more complex compounds like naphthalene.

An electronic formula has also been proposed, in which the electrons are symmetrically distributed among the carbon atoms, but this idea has now been modified in favour of a more complex redistribution of electrons in the whole molecule, resulting in an increase of stability. Such a composite structure is said to be due to *resonance* and is based on the modern theory of energy quanta. Many other resonance structures have been adopted for organic compounds (p. 538).

For practical purposes the fourth carbon bond may be omitted from the formula, and until something more definite transpires concerning it, the simple hexagon formula will suffice.

THE AROMATIC HYDROCARBONS

Distillation of Coal-Tar.—The principal source of benzene and its homologues is coal-tar. Coal-tar is produced in the manufacture of coal-gas by the destructive distillation of coal in fire-clay retorts. The gases from the retorts pass through a series of upright pipes or air-condensers, which rise from a long trough in which the tar collects, whence it is drawn into a tank, or tar-well. Tar is also produced in considerable quantities in the manufacture of coke in coke-ovens. The quantity of tar varies with the character of the coal employed, 10 to 20 gallons being usually obtained from each ton of coal. When the tar is submitted to fractional distillation, it yields a variety of volatile products of different boiling-points, which form the material from which the majority of aromatic compounds are prepared.

Although the tar contains the bulk of the benzene hydrocarbons, a certain amount of the latter is present in the coal and coke-oven gases. The gases are now scrubbed, *i.e.* passed through an absorbent such as creosote oil, which removes these valuable hydrocarbons, which are recovered by distillation.

used for dissolving rubber in the preparation of waterproof fabrics, and *burning naphtha*, for illuminating purposes.

The 50 or 90 per cent. benzene, by a second distillation, is separated into benzene, toluene, and xylene.[1]

Benzene, C_6H_6, was discovered by Faraday (1825). Before the introduction of coal-gas, a little illuminating gas was manufactured from oil, and delivered to consumers compressed into cylinders. By cooling the gas from these cylinders in a freezing mixture, a liquid was obtained from which Faraday separated benzene by distillation. Benzene was afterwards obtained by distilling calcium benzoate with slaked lime. The benzoate decomposes into benzene and calcium carbonate, a process which recalls the formation of marsh-gas from sodium acetate[2]—

$$\underset{\text{Calcium benzoate.}}{C_6H_5\boxed{COOca' + ca'O}H} = \underset{\text{Benzene.}}{C_6H_6} + CaCO_3.$$

EXPT. 134.—Grind together 30 grams of calcium benzoate with twice its weight of soda-lime, and distil the mixture from a retort, which must be attached to a condenser and receiver. Water and a light brown oil distil, smelling strongly of benzene. The benzene can be separated from the water by a small tap-funnel. It is then dried over calcium chloride and redistilled.

Benzene has been synthesised by Berthelot from acetylene (p. 262), by heating the gas in a closed vessel at a moderately low temperature. The acetylene polymerises, and forms benzene—

$$\underset{\text{Acetylene.}}{3C_2H_2} = \underset{\text{Benzene.}}{C_6H_6}.$$

Benzene is obtained principally from coal-tar, but a certain amount is also recovered from coke oven gas.

The commercial product always contains a small quantity of an organic sulphur compound, known as *thiophene*, C_4H_4S, which is a colourless liquid and has nearly the same boiling-point as benzene (p. 564). The presence of thiophene may be shown in the following way: Dissolve a crystal of isatin (p. 528) in the cold in a few c.c. of strong sulphuric acid and add about the same volume of coal-tar benzene. On shaking, a deep blue coloration (indophenin) is produced. If the benzene obtained from calcium benzoate is treated in the same manner no blue colour is developed.

[1] The commercial names are benzol, toluol, and xylol.
[2] The symbol ca′ represents half the bivalent ion Ca″ (p. 129).

EXPT. 135.—The distillation of coal on a small scale may be shown by means of the apparatus, Fig. 61, p. 160. A copper vessel *a* containing coal in small lumps is fixed to a doubly-tubulated vessel *b*, which is in turn attached to a condenser *c*, and wash-bottle containing caustic soda solution *d*. A delivery tube conducts the inflammable gases into an inverted cylinder *e*. The tar and water accumulate in *b*.

Properties of Benzene.—Benzene is a colourless liquid with a peculiar smell. It boils at 80·5°, solidifies at 5·4°, and has a specific gravity of 0·874 at 20°. It is very inflammable, and burns with a luminous and smoky flame. It is insoluble in water, and, having a lower specific gravity, floats on the surface. It is sometimes used like ether for separating organic liquids when mixed with water, also for extracting fats, etc., for dry cleaning and for motor fuel.

The chemical properties of benzene may be taken as typical of the family of aromatic hydrocarbons. Benzene resists the action of all the ordinary oxidising and reducing agents. Strong hydriodic acid, at a high temperature, and after prolonged heating, or hydrogen in presence of colloidal platinum at the ordinary temperature, or finely divided nickel at about 160°, converts it into the *hexahydride*, C_6H_{12}. When benzene is exposed to the action of chlorine or bromine in sunlight, crystals of *benzene hexachloride*, $C_6H_6Cl_6$, or *hexabromide*, $C_6H_6Br_6$, are slowly deposited.

EXPT. 136.—Place a little bromine in a beaker and cover it with benzene. Expose the beaker in a small desiccator to sunlight for a few days when crystals of the hexabromide will be deposited.

Both substances are very unstable, and emit a smell of chlorine or bromine. Potash decomposes them at once into trichloro- and tribromo-benzene—

$$\underset{\text{Benzene hexachloride.}}{C_6H_6Cl_6} + 3KOH = \underset{\text{Trichlorobenzene.}}{C_6H_3Cl_3} + 3KCl + 3H_2O.$$

If chlorine or bromine acts upon benzene in presence of a "carrier," substitution occurs, and a series of chlorinated or brominated products is formed, containing from one up to six atoms of the halogen in place of hydrogen—

$$C_6H_6 + Cl_2 = \underset{\text{Monochlorobenzene.}}{C_6H_5Cl} + HCl, \qquad C_6H_5Cl + Cl_2 = \underset{\text{Dichlorobenzene.}}{C_6H_4Cl_2} + HCl,$$

and so forth.

EXPT. 137.—Pour a few c.c. of benzene into four test-tubes, and add a few drops of bromine to each. Into one of the test-tubes drop a small piece of aluminium-mercury couple (p. 70), into a second pour a few drops of pyridine and warm gently, and to a third add some iron filings. Notice the difference in the action as indicated by the evolution of hydrobromic acid from the four test-tubes.

Iodine has no direct action on the aromatic hydrocarbons unless at a high temperature and with the addition of iodic acid, nitric acid or sodium persulphate, $Na_2S_2O_8$. The latter serve to decompose the hydriodic acid formed in the reaction, which would otherwise produce a reversal of the process—

$$5HI + HIO_3 = 3I_2 + 3H_2O.$$

This action of the halogens on benzene recalls their behaviour with the paraffins (p. 65).

Dilute nitric acid has no action on benzene, but strong nitric acid rapidly attacks it, and forms nitro-derivatives. The action is assisted by the presence of strong sulphuric acid, which absorbs the water formed in the process—

$$C_6H_6 + HNO_3 = \underset{\text{Nitrobenzene.}}{C_6H_5{\cdot}NO_2} + H_2O.$$

$$C_6H_5NO_2 + HNO_3 = \underset{\text{Dinitrobenzene.}}{C_6H_4{:}(NO_2)_2} + H_2O.$$

EXPT. 138.—Mix together 20 c.c. of strong sulphuric acid and 15 c.c. of strong nitric acid in a graduated cylinder. Add half the volume of the mixed acid (17 c.c.) gradually to 5 c.c. of benzene, contained in a small flask; cool and shake well. Heat is evolved and nitrobenzene is formed. When the acid has been added, pour a little into water and notice that the liquid has a yellow colour, and, instead of floating on the surface like benzene, sinks in the water. Add the remainder of the acid at once to the remaining liquid in the flask, and heat for a quarter of an hour on the water-bath; then pour into a cylinder of water. The substance which now separates is no longer liquid; but a yellow, crystalline solid, which is the dinitro-compound.

Strong sulphuric acid, on warming, gradually dissolves benzene and forms benzene sulphonic acid. Fuming sulphuric acid converts the latter into benzene disulphonic acid—

$$C_6H_6 + H_2SO_4 = \underset{\text{Benzene sulphonic acid.}}{C_6H_5{\cdot}SO_3H} + H_2O.$$

$$C_6H_5{\cdot}SO_3H + H_2SO_4 = \underset{\text{Benzene disulphonic acid.}}{C_6H_4(SO_3H)_2} + H_2O.$$

EXPT. 139.—Mix together in a boiling-tube about 3 c.c. of benzene and 10 c.c. of strong sulphuric acid, and heat gently with constant shaking. The benzene, which at first floats on the acid, gradually dissolves with rise of temperature. When a little of the mixture is poured into water, a clear solution of benzene sulphonic acid is obtained. If another portion is poured into about four times its volume of saturated salt solution, crystalline plates of sodium benzene sulphonate, $C_6H_5 \cdot SO_3Na$, separate.

The action of strong nitric and sulphuric acids on benzene, in producing nitro-derivatives in the one case, and sulphonic acids in the other, is a characteristic property of aromatic compounds. The homologues of benzene, as well as the majority of benzene derivatives, react with these two acids in the manner described. In this respect the aromatic compounds offer a marked contrast to the paraffins, and the other aliphatic hydrocarbons. Reference should be made to the methods by which nitro-paraffins (p. 192), and the aliphatic sulphonic acids (p. 197), are produced.

Toluene, *Methyl benzene*, *Phenyl methane*, $C_6H_5 \cdot CH_3$.—Toluene received its name from a resin, known as Tolu balsam, from which it is obtained by distillation. It is now separated by fractional distillation from coal-tar naphtha by the method already described. Toluene closely resembles benzene in properties. It is a liquid with an odour resembling that of benzene. It boils at 110°, solidifies at − 98° and has a sp. gr. 0·869 at 16°. The relation of toluene to benzene has been determined by analysis and synthesis. It has already been stated that toluene may be oxidised to benzoic acid, and the latter converted by distillation with lime into benzene. The synthetic processes used in its preparation are known as the methods of Fittig, and of Friedel and Crafts.

Fittig's method recalls that employed by Wurtz in the synthesis of the paraffins (p. 72). It consists in mixing together bromobenzene and methyl iodide, diluted with dry ether, and adding sodium in thin slices. The action commences spontaneously, and, when it ceases, the liquid is decanted from the sodium salts, and the toluene separated by fractional distillation—

$$\underset{\text{Bromo-benzene.}}{C_6H_5Br} + \underset{\text{Methyl iodide.}}{CH_3I} + 2Na = \underset{\text{Toluene.}}{C_6H_5 \cdot CH_3} + NaBr + NaI.$$

The Friedel-Crafts Reaction.—In this reaction anhydrous aluminium chloride is added to benzene, and methyl chloride

EXPT. 137.—Pour a few c.c. of benzene into four test-tubes, and add a few drops of bromine to each. Into one of the test-tubes drop a small piece of aluminium-mercury couple (p. 70), into a second pour a few drops of pyridine and warm gently, and to a third add some iron filings. Notice the difference in the action as indicated by the evolution of hydrobromic acid from the four test-tubes.

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The Friedel-Crafts Reaction.—In this reaction anhydrous aluminium chloride is added to benzene, and methyl chloride

passed in, or methyl bromide added to the mixture. Hydrochloric, or hydrobromic acid is rapidly evolved, and toluene is formed. The product is poured into water, and the upper layer removed and fractionated. The action of the aluminium chloride is not fully understood, but is usually accounted for by the formation of an intermediate compound of benzene and aluminium chloride, which is decomposed by the alkyl halide. The reaction may be expressed as follows—

$$C_6H_6 + CH_3Cl\ [+ AlCl_3] = C_6H_5{\cdot}CH_3 + HCl.$$

By prolonging the action, additional methyl groups are introduced into benzene, and a series of di-, tri-, etc., methyl benzenes are formed.

Anhydrous aluminium chloride, unlike most metallic compounds, is soluble in ether, but it is very hygroscopic, as it combines with water to form the hexahydrate, which is useless for this reaction.

Both Fittig's and the Friedel-Crafts reactions can be applied to the synthesis of a large number of aromatic hydrocarbons by substituting different alkyl halides for the methyl compounds. The Friedel-Crafts method in particular has a very wide and varied application, for its action is not limited to the production of hydrocarbons alone. Many other substances containing chlorine, such as the acid chlorides, react in presence of aluminium chloride with benzene and its homologues, with the evolution of hydrochloric acid and the formation of new products. The acid chlorides yield ketones. Benzene, acetyl chloride, and aluminium chloride form phenyl methyl ketone—

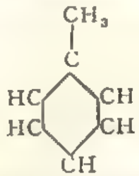
$$C_6H_6 + CH_3{\cdot}CO{\cdot}Cl\ [+ AlCl_3] = \underset{\text{Phenyl methyl ketone.}}{C_6H_5{\cdot}CO{\cdot}CH_3} + HCl.$$

It appears that only hydrocarbons of the aromatic series can enter into these reactions. Neither the paraffins nor olefines possess the property. The Friedel-Crafts reaction is, therefore, recognised as a distinctive feature of the aromatic hydrocarbons.

EXPT. 140.—Pour a few c.c. of benzene into a test-tube; add about a gram of anhydrous aluminium chloride and then a few drops of ethyl bromide. Hydrobromic acid is at once evolved. If the product is poured into water, the upper layer contains ethyl benzene, which, on

a larger scale, would be separated by fractional distillation. Repeat the experiment, using acetyl chloride in place of ethyl bromide, and pour the product into caustic soda solution. The upper layer contains methyl phenyl ketone, which possesses a characteristic smell.

Structure of Toluene.—The synthesis of toluene from benzene clearly explains its structure. Toluene is the methyl derivative of benzene, the graphic formula of which is represented as follows—



Structural formula for Toluene.

Toluene is also known as phenyl methane. The term **phenyl** denotes the univalent radical $C_6H_5{}'$ of benzene, just as ethyl, $C_2H_5{}'$, stands for the radical of ethane. The name is derived from the Greek φαίνω, to illuminate, from the connection of benzene with the coal-gas manufacture.[1] It is equally correct to represent toluene as methane in which a phenyl group replaces an atom of hydrogen $CH_3{\cdot}C_6H_5$.

Nucleus and Side-chain.—It is found convenient to draw a distinction between the purely aromatic part, or ring, and the aliphatic part, or alkyl group, in a compound like toluene. The aromatic or benzenoid part is known as the *nucleus,* whilst the aliphatic part is denoted by the term *side-chain.* We say that toluene contains a nucleus and a side-chain.

A peculiarity of the side-chain is the effect produced upon it by oxidising agents. This has already been referred to (p. 381). The side-chain is converted into a carboxyl group, the nucleus remaining intact. Toluene forms benzoic acid. The same result is produced if the side-chain is an ethyl, propyl, or other alkyl group, containing several carbon atoms; and when two or more side-chains are present each of them is oxidised in the same way to a carboxyl group. The value of this property in studying the

[1] The generic term for the aromatic radicals is *aryl,* which corresponds to alkyl of the aliphatic series.

structure of aromatic hydrocarbons and their derivatives is very considerable, and is well illustrated in the case of the xylenes (p. 396).

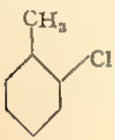
Action of Chlorine on Toluene.—Toluene, like benzene, undergoes substitution by chlorine and bromine. Substitution is not, however, limited to the nucleus. Hydrogen may be replaced in the side-chain. Substitution takes place in the side-chain if chlorine is passed into boiling toluene, and the following three products are successively produced—

$C_6H_5{\cdot}CH_2Cl$	$C_6H_5{\cdot}CHCl_2$	$C_6H_5{\cdot}CCl_3$.
Benzyl chloride.	Benzylidene chloride or Benzal chloride.	Benzenyl chloride, or Benzotrichloride.

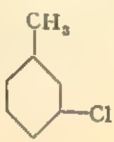
The first contains the univalent radical benzyl, $C_6H_5{\cdot}CH_2'$, corresponding to ethyl; the second benzylidene, $C_6H_5{\cdot}CH''$, corresponding to ethylidene; the third, the radical benzenyl, $C_6H_5{\cdot}C'''$.

If, on the other hand, chlorine is passed into cold toluene to which a little antimony chloride, aluminium-mercury couple, iodine, or other carrier, is added, substitution is confined to the nucleus, and mono-, di-, tri-, etc., chlorotoluenes are formed.

There are three monochlorotoluenes, the ortho-, meta-, and para-compounds, which are isomeric with benzyl chloride, so that there are in all four compounds of the formula C_7H_7Cl. In the following formulæ the carbon and hydrogen atoms of the nucleus are omitted—

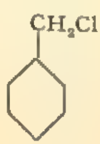


Ortho-chlorotoluene.



Meta-chlorotoluene.

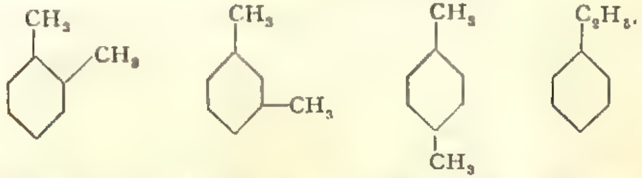
Para-chlorotoluene.



Benzyl chloride.

There is a marked difference in the properties of the halogen derivatives of the aromatic hydrocarbons containing the halogen in the side-chain and those which are substituted in the nucleus: but the subject will be reserved for a later chapter (p. 404).

Hydrocarbons of the Formula, C_8H_{10}.—Theory requires four isomeric hydrocarbons of the formula C_8H_{10}, viz., ortho-, meta-, and para-dimethylbenzene and an ethyl benzene—



Ortho-dimethylbenzene. Meta-dimethylbenzene. Para-dimethylbenzene. Ethyl-benzene.

The three dimethylbenzenes, which are termed **xylenes,** are all present in coal-tar, the meta-compound largely predominating. They cannot be separated by fractional distillation, as the boiling-points lie too close together, and commercial xylene is therefore a mixture of the three isomers.

	Boiling-point.
Ortho-xylene	142°
Meta-xylene	137°
Para-xylene	137°

Meta-xylene is readily separated from the other two compounds by boiling with dilute nitric acid, which oxidises the ortho- and para-compounds more rapidly than the meta-, and converts them into acids. The acids are then removed by shaking with caustic soda solution. The para-compound is separated by shaking with strong sulphuric acid, which dissolves the ortho- and meta-compounds in the form of their sulphonic acids. A simpler process for obtaining pure para- and ortho-xylene is by synthesis.

The constitution of all four compounds has been determined by synthesis. The ortho- and para-xylenes have been prepared by Fittig's reaction from ortho- and para-bromotoluene, methyl iodide, and sodium—

$$C_6H_4Br(CH_3) + CH_3I + 2Na = C_6H_4(CH_3)_2 + NaBr + NaI.$$

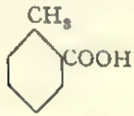
By means of the Friedel-Crafts reaction, using benzene methyl chloride and aluminium chloride, the same two compounds are formed, but the ortho-compound predominates. Pure meta-xylene cannot be prepared by either of these methods, but is

obtained from mesitylene (p. 397), which on oxidation gives mesitylenic acid. The acid, when distilled with lime, yields meta-xylene—

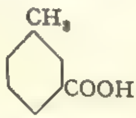
$$\underset{\text{Mesitylenic acid.}}{C_6H_3(CH_3)_2{\cdot}COOH} = \underset{\text{Meta-xylene.}}{C_6H_4(CH_3)_2} + CO_2.$$

Ethyl benzene is readily prepared from bromobenzene, ethyl iodide, and sodium, or by the Friedel-Crafts method from benzene, ethyl bromide, and aluminium chloride (Expt. 140, p. 392).

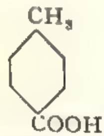
Oxidation of the Xylenes, etc.—The behaviour of the four compounds on oxidation is instructive, as illustrating the manner in which the constitution of an aromatic hydrocarbon may be studied. When the hydrocarbon is oxidised, the side-chains are converted into carboxyl groups as already explained. Ethyl benzene gives benzoic acid, and consequently contains one side-chain. The xylenes, on the other hand, yield dibasic acids containing two carboxyl groups. The process occurs in two stages; the two methyl groups being converted successively into carboxyl groups. The first products are known as toluic acids—



Ortho-toluic acid.

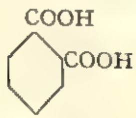


Meta-toluic acid.

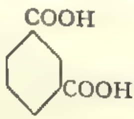


Para-toluic acid.

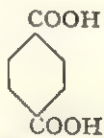
Each of these gives rise to a dibasic acid, known respectively as phthalic, isophthalic, and terephthalic acids—



Phthalic acid.



Isophthalic acid.



Terephthalic acid.

The three toluic acids and the esters of the three phthalic acids [1] have different melting-points, by which they may be readily identified. Let us suppose that a hydrocarbon of unknown com-

[1] The acids themselves either decompose or sublime on heating.

position yields benzoic acid on oxidation; natural inference is that it contains a single side-chain. The formation of one of the phthalic acids implies the presence of two side-chains, whilst the melting-point of the acid will indicate their relative positions. Moreover, by this process of oxidation the side-chains may be successively removed. The three toluic acids, by distillation with lime, give toluene; the three phthalic acids form benzene. In this way the nature, the position, and the number of the side-chains may be determined.

It must not be inferred that the process of oxidation of side-chains takes place with equal facility in the case of the three xylenes or other group of isomeric hydrocarbons. Considerable differences have been observed, not only in the case of different isomers, but in the effect upon them of different oxidising agents. Dilute nitric acid is the least active oxidising agent of those usually employed. The three xylenes are converted by nitric acid into toluic acids, whilst chromic acid solution oxidises meta- and para-xylene to the corresponding phthalic acids. On the other hand, the ortho-compound is completely decomposed by chromic acid, whilst potassium permanganate oxidises it to phthalic acid. These results are intimately related with the protective influence which groups in close proximity exert upon one another. The presence of groups in the ortho-position to the methyl group renders oxidation more difficult. We shall be frequently confronted with similar cases of protective influence, or, as it is sometimes termed, *space interference* or *steric hindrance* exercised by adjoining groups in arresting, or impeding chemical change (p. 489).

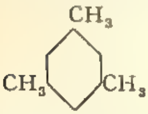
Hydrocarbons of the Formula C_9H_{12}.—Isomeric hydrocarbons of the formula C_9H_{12} include three trimethylbenzenes, three methylethylbenzenes, a propyl- and an isopropylbenzene.

Mesitylene, or 1-3-5-*Trimethylbenzene.*—The formation of mesitylene from acetone and sulphuric acid has already been described (p. 144). A similar reaction occurs with methyl acetylene, $CH_3 \cdot C⋮CH$, which polymerises in presence of sulphuric acid. The latter reaction resembles the formation of benzene from acetylene (p. 388)—

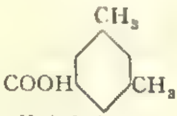
$$\underset{\text{Methyl acetylene.}}{3CH_3 \cdot C⋮CH} = \underset{\text{Mesitylene.}}{C_6H_3(CH_3)_3}.$$

These reactions are of interest as affording grounds for the assumption of a symmetrical formula for mesitylene, a view which

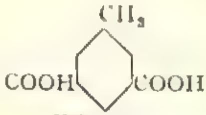
is confirmed by experimental evidence. Mesitylene yields a series of acids on oxidation, which are known as mesitylenic, uvitic, and trimesic acids—



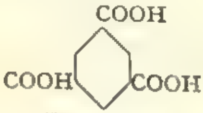
Mesitylene.



Mesitylenic acid.



Uvitic acid.



Trimesic acid.

Each of the acids loses carbon dioxide on distillation with lime, so that mesitylene may be converted in succession into *m*-xylene, toluene, and benzene. Mesitylene is a colourless liquid which boils at 165°.

Pseudocumene, or 1-2-4-*Trimethylbenzene,* is one of the constituents of solvent naphtha (p. 387), from which it may be separated first by fractional distillation and then by treatment with sulphuric acid, which dissolves the pseudocumene. The sulphuric acid solution is then distilled in steam (p. 417), when the pseudocumene passes over. It is a colourless liquid which boils at 169°.

Cumene, or *Isopropylbenzene,* $C_6H_5 \cdot CH(CH_3)_2$, is prepared from cumic acid, $COOH \cdot C_6H_4 \cdot CH(CH_3)_2$, by distillation with lime or by one of the synthetic methods described above (p. 391).

Cymene, *p-Cymene,* or *p-Methylisopropylbenzene,*

$$CH_3 \cdot C_6H_4 \cdot CH(CH_3)_2,$$

is the most important hydrocarbon of the formula $C_{10}H_{14}$. It is found in certain essential oils, such as oil of thyme and eucalyptus oil, and it is closely related to camphor, $C_{10}H_{16}O$ (p. 508), and to the group of hydrocarbons of the formula $C_{10}H_{16}$, known as terpenes, of which turpentine oil is the best known example (p. 506). Cymene is usually obtained from camphor by distillation with phosphorus pentoxide or pentasulphide, which act as dehydrating agents—

$$\underset{\text{Camphor.}}{C_{10}H_{16}O} = \underset{\text{Cymene.}}{C_{10}H_{14}} + H_2O,$$

or from turpentine by the action of iodine or strong sulphuric acid, whereby the oil is oxidised—

$$C_{10}H_{16} + O = C_{10}H_{14} + H_2O.$$

Cymene boils at 175°. On oxidation it yields *p*-toluic and terephthalic acids. There are consequently two side-chains in the para-position, one of which is a methyl group. The character of the other group has been determined by synthesis. *m*-Cymene is also known, and appears to be the parent-substance of a certain number of terpenes.

Symmetrical Structure of Benzene.—It has already been pointed out (p. 381) that Kekulé's theory of the structure of benzene rests mainly on evidence of an indirect or negative character—the non-existence of more than one mono-derivative; the occurrence of not more than three di-derivatives. The theory is in so far inconclusive, that future research might bring to light a second mono- or an additional di-derivative, when the theory would fall to the ground. The symmetrical structure of benzene, however, rests upon the firmer basis of direct experiment. The experimental method involves a principle, first employed by Hübner and Petermann, which the following example may serve to illustrate. By the action of nitric acid on benzoic acid, the three isomeric compounds *o*-, *m*-, and *p*-nitrobenzoic acids are formed. When each of these is distilled with lime, the same nitrobenzene is produced. The difference in the three nitrobenzoic acids must be ascribed to a different position of the three nitro-groups in the benzene ring; but seeing that the products obtained by removal of the carboxyl group are identical, the three positions of the nitro-groups must be similarly situated. This may be represented as follows:

	a b c d e f
Benzene	C_6H H H H H H
Benzoic acid	C_6H H H H H COOH

Nitrobenzoic acids.		Nitrobenzene.
$C_6(NO_2)$H H H H COOH	$\longrightarrow$	$C_6(NO_2)$H H H H H
C_6H(NO_2)H H H COOH	$\longrightarrow$	C_6H(NO_2)H H H H
C_6H H(NO_2)H H COOH	$\longrightarrow$	C_6H H(NO_2)H H H

O

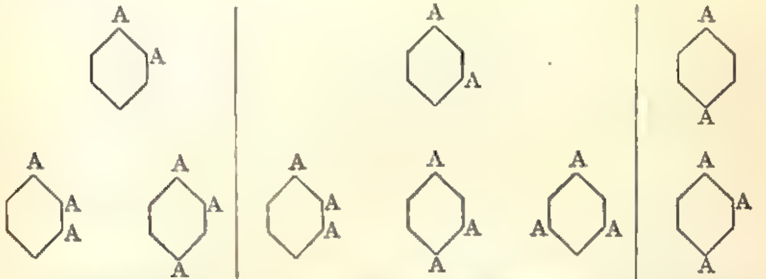
The structure of benzene must therefore be symmetrical as regards the three carbon atoms, *a*, *b*, *c*, to which the nitro-groups are attached. The same process has been applied to all six carbon atoms with the same result, and the complete symmetry of the molecule has thus been established.

Orientation.—The existence of three di-derivatives, the ortho-, meta-, and para-compounds of benzene, has been repeatedly mentioned. They are distinguished by differences of melting- or boiling-point, sometimes by chemical properties, and occasionally, if solid, by their crystalline form. Tri-derivatives in which the three substituting elements or groups are the same, as in the trimethylbenzenes, likewise form three isomers; if two of the groups are the same and the third is different, six isomers are possible and in many cases known, whilst, if all three groups are different, the number of possible isomers rises to ten and so forth.

Is there any means of assigning to the different isomers the relative positions in the nucleus of the substituting elements or groups? To take the simplest case, that of the di-derivatives: Is there any means of determining which of the three isomers is the ortho-, which the meta-, and which the para-compound? The process by which this is accomplished is known as *orientation* (French, *orienté*, situated).

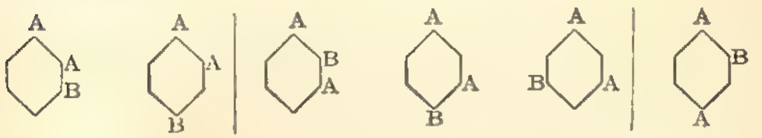
Provided the position of the groups in certain fundamental compounds is known, the structure of substances directly related to them would naturally follow. If, for example, the positions of the carboxyl groups in the three phthalic acids could be ascertained, that of the methyl groups in the three xylenes would be known (p. 395). At first the structure of certain fundamental compounds rested largely upon assumptions, which, being frequently incorrect, led to much confusion. The process known as **Körner's absolute method** of orientation is free from any such objection. It is based upon the following principle. A di-derivative will yield a different number of tri-derivatives according to whether the original substance is an ortho-, meta-, or para-compound. If it can be shown, for example, that one of the three isomeric dichlorobenzenes can be converted into three trichlorobenzenes or three dichloro-nitrobenzenes, it can only happen if the original dichlorobenzene is a meta-compound.

In the same way, if the di-derivative can only give two tri-derivatives, it is an ortho-compound, whilst a para-compound is only capable of yielding one tri-derivative. This will be understood from the following scheme, in which A stands for the element or group—

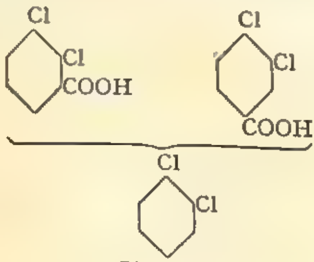


Ortho gives two tri-derivatives. Meta gives three tri-derivatives. Para gives one tri-derivative.

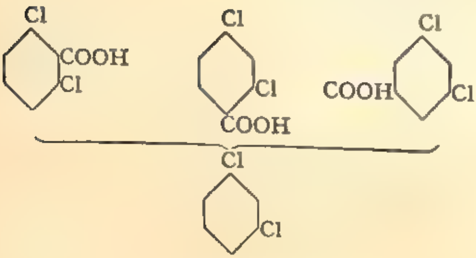
It is immaterial whether the new element or group is the same as the other two or not; the rule still holds. The only difference lies in this, that if all three groups are the same, the total number of isomeric tri-derivatives is three; if the new group (B) is different from the other two, each of the six products represents a different substance—



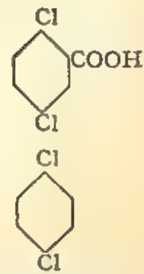
In practice, the above method of determining the structure of aromatic compounds is difficult to carry out, as the whole series of derivatives cannot always be directly prepared. The reverse process may sometimes be adopted with advantage. There are, for example, six dichlorobenzoic acids, which when distilled with lime give three dichlorobenzenes. The dichlorobenzene obtained from three of the dichlorobenzoic acids is a meta-compound; that obtained from two of the acids is an ortho-compound. The sixth dichlorobenzoic acid gives a para-compound.



o-Dichlorobenzene.



m-Dichlorobenzene.



p-Dichlorobenzene.

Questions on Chapter XXV

1. Explain the origin and present meaning of the term *aromatic compounds*. Name some of the facts which originated the view of a common nucleus in these compounds.

2. Explain why benzoic acid is said to be a benzene derivative. What relation does oil of bitter almonds bear to benzoic acid?

3. Discuss the merits and demerits of Kekulé's formula for benzene, and those of any alternative formula.

4. Give an outline of the production of aromatic hydrocarbons from coal-tar.

5. By what physical and chemical properties are benzene and its homologues distinguished from all other hydrocarbons?

6. Discuss the structural formula of toluene.

7. Give an account of the principal reactions of toluene which prove that it contains both a benzenoid and a paraffinoid residue. Describe precisely how you would conduct the operations and isolate the products.

8. Describe the Friedel-Crafts and Fittig reactions for obtaining benzene hydrocarbons. Give at least one other example of the application of each of these important general methods of preparation.

9. How would you proceed to (1) identify an aromatic hydrocarbon? (2) remove it from a mixture with petroleum?

10. State how you would distinguish the isomeric hydrocarbons of the formula C_8H_{10}. How would you show that they are all derivatives of benzene?

11. Give the formulæ of the isomeric xylenes, and state how one of them may be converted into phthalic acid and how another may be made from mesitylene.

12. Give the structural formula of mesitylene: explain the evidence upon which this formula is based and its significance in ascertaining the constitution of derivatives of benzene.

13. By what means has orientation in benzenoid compounds been determined?

14. Three dichlorobenzoic acids, when distilled with lime, yield the same dichlorobenzene. Formulate the reaction and deduce from it the structure of the dichlorobenzene produced.

15. What experimental proof exists that the hydrogen atoms in benzene are of equal value and have similar functions?

CHAPTER XXVI

AROMATIC HALOGEN COMPOUNDS

The Halogen Substitution Products.—The action of the halogens on the aromatic hydrocarbons in producing substitution has already been described (p. 394), and it was then pointed out that, by modifying the conditions, the replacement of hydrogen by chlorine, or bromine, may occur in the side-chain or be confined to the nucleus. The process of substitution by chlorine, or bromine, is usually termed *chlorination* or *bromination*.

In addition to this method, the action of phosphorus pentachloride, or pentabromide, on hydroxy-compounds may be employed, though rarely used. The method resembles the action of the phosphorus halides on the aliphatic alcohols. Hydroxybenzene, or ordinary phenol, gives chloro- or bromo-benzene—

$$\underset{\text{Phenol.}}{C_6H_5(OH)} + PCl_5 = \underset{\text{Chlorobenzene.}}{C_6H_5Cl} + POCl_3 + HCl.$$

The same reaction occurs if the hydroxyl group is in the side-chain, as in benzyl alcohol, which forms benzyl chloride—

$$\underset{\text{Benzyl alochol.}}{C_6H_5{\cdot}CH_2(OH)} + PCl_5 = \underset{\text{Benzyl chloride.}}{C_6H_5{\cdot}CH_2Cl} + POCl_3 + HCl.$$

A much more important means of introducing all three halogens into the nucleus is by replacing the amino group of the aromatic amines by the aid of the *diazo-reaction*, a process which is of sufficient importance to merit a chapter to itself (p. 432). It is therefore postponed for the present. The following examples are selected in order to illustrate the formation of the halogen derivatives by direct substitution.

Monochlorobenzene, *Phenyl chloride,* C_6H_5Cl.—Dry chlorine is passed into benzene, to which a small piece of aluminium-mercury couple (p. 70) is added as carrier. Hydrochloric acid is evolved, and when the additional weight corresponding to the replacement of one atom of hydrogen by chlorine has been gained,

the operation is stopped. The liquid is shaken with a solution of caustic soda, then dehydrated over calcium chloride, and finally distilled, the portion boiling at 130°–135° being collected. Chlorobenzene is a colourless liquid, which boils at 132°. Like benzene, it forms nitro- and sulphonic acid derivatives when acted upon with strong nitric or sulphuric acid.

Bromobenzene, or *Phenyl bromide*, C_6H_5Br, is formed in the same way, the bromine being added slowly to the benzene containing the aluminium-mercury couple. Both chloro- and bromo-benzene may be prepared by the diazo-reaction from amino-benzene, $C_6H_5NH_2$. This method is the only available one for the preparation of *iodobenzene*, C_6H_5I, as direct substitution by iodine is difficult to effect (p. 390).

The following are the boiling-points and specific gravities of the three compounds, from which it will be seen that with increasing molecular weight there is a rapid rise in both boiling-point and specific gravity :—

		Boiling-point.	Specific gravity.
Chlorobenzene	C_6H_5Cl	132°	1·128
Bromobenzene	C_6H_5Br	155°	1·517
Iodobenzene	C_6H_5I	188°	1·861

Chlorotoluenes, *Tolyl chlorides*, $C_6H_4(CH_3)Cl$, exist in three isomeric forms, the ortho-, meta-, and para-compounds. The ortho- and para-compounds are formed by chlorinating toluene in presence of a carrier. They are all obtained in a pure state from the corresponding amino-toluenes, $C_6H_4(CH_3)NH_2$, by the diazo-reaction already referred to. They are colourless liquids, resembling chlorobenzene.

The chlorotoluenes are rapidly converted, on oxidation, into the corresponding chlorobenzoic acids, by the melting-points of which they are easily identified.

	Boiling-point.		Melting-point.
o-Chlorotoluene	156°	*o*-Chlorobenzoic acid	137°
m- ,,	150°	*m*- ,,	153°
p- ,,	163°	*p*- ,,	240°

The chlorination or bromination of xylene and the higher methyl derivatives of benzene is accomplished in many cases without the

use of a carrier. The presence of methyl groups seems generally to facilitate the action of reagents on the benzene nucleus.

Benzyl chloride, $C_6H_5{\cdot}CH_2Cl$, is isomeric with the chlorotoluenes. It is manufactured by passing dry chlorine into boiling toluene, until it has attained the requisite specific gravity. In the laboratory the end of the operation is ascertained from the increase in weight. The product is then fractionated. Benzyl chloride is a colourless liquid which boils at 176°.

Benzal chloride, *Benzylidene chloride*, $C_6H_5{\cdot}CHCl_2$, is prepared in the same manner as benzyl chloride, but the action of the chlorine is prolonged until a second atom of chlorine is introduced. Benzal chloride resembles benzyl chloride, but boils at 206°. It is used commercially for the preparation of benzaldehyde (pp. 408, 475).

Benzo-trichloride, *Phenyl chloroform*, $C_6H_5{\cdot}CCl_3$, is the final product obtained by the chlorination of boiling toluene. It boils at 213°, and is converted into benzoic acid by heating with milk of lime, or water under pressure (p. 487).

Properties of the Halogen Derivatives.—All the halogen derivatives of the aromatic hydrocarbons, like those of the aliphatic series, are colourless liquids, or solids, specifically heavier than water, in which they are insoluble. They can be distilled without decomposition. Apart from these general characteristics, a considerable difference in properties is exhibited by the halogen compounds substituted in the nucleus and those which contain the halogen in the side-chain. Those substituted in the nucleus have an agreeable odour, whereas those which are substituted in the side-chain possess a pungent smell and attack the eyes. Benzyl chloride may be readily distinguished in this way from the isomeric chlorotoluenes.

Moreover, the nuclear halogen compounds are very stable substances. Unlike the aliphatic halogen compounds, the halogen atom is firmly fixed in the molecule, *e.g.* bromobenzene is quite unaffected by most of the reagents which act upon ethyl bromide.

EXPT. 141.—This may be shown by shaking bromo- or iodo-benzene in one test-tube and methyl iodide in another with an alcoholic solution of silver nitrate. The latter only is decomposed, and gives a precipitate of silver halide. On the other hand, they combine like the alkyl halides with magnesium to form Grignard reagents, which behave like aliphatic compounds (p. 242).

The stability of the nuclear halogen atom is greatly weakened by the presence of nitro-groups in the ortho- or para-position. The halogen, in a substance like dinitrochlorobenzene, is readily replaced by hydroxyl by boiling with caustic potash solution, or by the amino-group by the action of ammonia, dinitrohydroxybenzene, $C_6H_3(NO_2)_2OH$, and dinitroaminobenzene, $C_6H_3(NO_2)_2NH_2$ being formed.

The side-chain halogen compounds, on the other hand, closely resemble the alkyl halides; indeed, broadly speaking, all compounds substituted in the side-chain, whatever may be the substituting element or group, bear a close resemblance in chemical properties to the corresponding aliphatic compounds. In the present case, the halogen atom is replaceable by hydroxyl, ethoxyl, amino, cyanogen, nitro, etc., groups by the action of such reagents as are enumerated on p. 83.

Benzyl chloride yields the following series of products by the action of potash, ammonia, and potassium cyanide :—

$$C_6H_5\cdot CH_2Cl + KOH = \underset{\text{Benzyl alcohol}}{C_6H_5\cdot CH_2OH} + KCl.$$

$$C_6H_5\cdot CH_2Cl + 2NH_3 = \underset{\text{Benzylamine.}}{C_6H_5\cdot CH_2NH_2} + NH_4Cl.$$

$$C_6H_5\cdot CH_2Cl + KCN = \underset{\text{Benzyl cyanide.}}{C_6H_5\cdot CH_2CN} + KCl.$$

Distinction between Nuclear and Side-chain Substitution Products.—It is a simple matter, from what has been stated above, to discover if the halogen has entered the side-chain or nucleus, and how far substitution has taken place in these two parts of the molecule. If the substance is oxidised, the side-chain (more readily if substituted) is converted into carboxyl, and an acid is formed. Any residual halogen atoms in the product must have been present in the *nucleus* of the original substance. For example, benzyl chloride yields benzoic acid, but chlorotoluene gives chlorobenzoic acid—

$$C_6H_5\cdot CH_2Cl + O_2 = \underset{\text{Benzoic acid.}}{C_6H_5\cdot COOH} + HCl.$$

$$C_6H_4Cl\cdot CH_3 + 3O = \underset{\text{Chlorobenzoic acid.}}{C_6H_4Cl\cdot COOH} + H_2O.$$

Moreover, by boiling with water, or alkalis, the halogen of the nucleus is undisturbed, but that of the side-chain is rapidly removed, and replaced by hydroxyl. Benzyl chloride, benzal

chloride, and benzo-trichloride give respectively benzyl alcohol, benzaldehyde, and benzoic acid—

$$C_6H_5CH_2\boxed{Cl + H}OH = \underset{\text{Benzyl alcohol.}}{C_6H_5{\cdot}CH_2(OH)} + HCl.$$

$$C_6H_5{\cdot}CHCl_2 + 2H_2O = \underset{\substack{\text{Intermediate product}\\\text{(not isolated).}}}{C_6H_5CH(OH)_2} + 2HCl \longrightarrow \underset{\text{Benzaldehyde.}}{C_6H_5{\cdot}CHO} + H_2O{\cdot}$$

$$C_6H_5{\cdot}CCl_3 + 3H_2O = \underset{\substack{\text{Intermediate product}\\\text{(not isolated).}}}{C_6H_5C(OH)_3} + 3HCl \longrightarrow \underset{\text{Benzoic acid.}}{C_6H_5{\cdot}COOH} + H_2O.$$

Positions taken by the Halogens entering the Nucleus.—In chlorinating (or brominating) benzene, the second chlorine (or bromine) atom enters the nucleus in the para-position, and, to a smaller extent, in the ortho-position to the first halogen atom. In chlorinating (or brominating) toluene, the first halogen enters the nucleus in both the ortho- and para-positions to the methyl group. Consequently a mixture of *o*- and *p*-chlorotoluene results; no trace of *m*-chlorotoluene is formed. The laws which determine the relative positions selected by the atoms or groups, when entering the nucleus, is a matter of considerable interest, and will be discussed more fully later (p. 412).

It should be observed that although the nuclear-substituted aryl halides are so stable that they are not decomposed when they are boiled with caustic alkalis in open vessels, separation of the halogen from the nucleus is nevertheless effected in the formation of Grignard reagents (p. 242) such as phenyl magnesium bromide.

Iodobenzene, C_6H_5I, combines with chlorine to form *iodobenzene dichloride,* $C_6H_5ICl_2$, when chlorine is passed into a well-cooled solution of iodobenzene in chloroform. The chlorine atoms are directly combined with the iodine atom, since the compound can be hydrolysed by dilute caustic soda solution to *iodosobenzene,* C_6H_5IO, a colourless solid which in aqueous solution liberates iodine from a dilute solution of hydriodic acid—

$$C_6H_5IO + 2HI = C_6H_5I + H_2O + I_2$$

When iodosobenzene is steam-distilled, a process of *autoxidation* occurs, part of the substance being oxidised to *iodoxybenzene,* $C_6H_5IO_2$, a non-volatile crystalline substance which explodes when heated.

QUESTIONS ON CHAPTER XXVI

1. Describe one method of preparing monochlorobenzene or monobromobenzene. Can iodobenzene be obtained by similar means? In what manner do these substances differ from aliphatic halides?

2. Describe the production of the mono-chloro-derivatives of toluene. How would you demonstrate the presence of chlorine in one of these compounds?

3. Three isomeric chlorotoluenes are known: how would you proceed to determine the position of the chlorine in relation to the methyl in each of these compounds?

4. What is the action of chlorine upon toluene under different conditions? Describe a process by which benzaldehyde may be produced from one of the resulting compounds.

5. Name and give the constitutional formulæ of the isomeric bodies possessing the molecular formula C_7H_7Cl. Describe at least one method of obtaining each, and suggest means for identifying them respectively.

6. How may toluene be converted into benzyl alcohol? Explain the difference in constitution between chlorotoluene and benzyl chloride.

7. What is the action of potash, ammonia, and potassium cyanide respectively on chlorobenzene and benzyl chloride? Are there any cases in which these reagents react on derivatives of chlorobenzene?

8. How would you determine whether chlorine had entered the side-chain or nucleus in a chlorine substitution product of an aromatic hydrocarbon? and how would you ascertain the number of chlorine atoms which had entered the benzenoid and paraffinoid portion of the molecule?

9. What rule determines the position taken by the halogens entering the nucleus?

CHAPTER XXVII

AROMATIC NITRO-COMPOUNDS

The Nitro-Compounds.—The nitro-derivatives of the aromatic hydrocarbons, and indeed of most aromatic compounds, are obtained by the method already described (p. 390), viz. by the action of nitric acid. The process is commonly known as *nitration*. The strength of the nitric acid is varied with the nature of the compound undergoing nitration; but in the case of the hydrocarbons it is expedient to employ a mixture of strong nitric acid (sp. gr. 1·4) and strong sulphuric acid. The first nitro-group is introduced into benzene and toluene with great ease, the second less readily, whereas to introduce the third, prolonged heating with fuming nitric acid (sp. gr. 1·5) and fuming sulphuric acid (sulphuric acid containing SO_3) is requisite. The nitration of the homologues of benzene, containing two or more methyl groups in the nucleus, is more easily accomplished; it is still further facilitated by the presence in the nucleus of hydroxyl and amino groups, so that in the latter case the reaction has to be carefully moderated.

Nitrobenzene, $C_6H_5NO_2$, is obtained by slowly running a mixture of strong nitric acid and strong sulphuric acid into well-cooled benzene, which is well shaken during the process—

$$C_6H_6 + HNO_3 = \underset{\text{Nitrobenzene.}}{C_6H_5{\cdot}NO_2} + H_2O.$$

When the acid has been added, the mixture is heated for a time on the water-bath to complete the reaction. The acid and nitrobenzene divide into two layers. The mixture is poured into a separating funnel, and the lower layer of acid withdrawn, after which the nitrobenzene is purified by shaking with caustic soda solution and then with water to remove any free acid. The nitrobenzene which forms the bottom layer is withdrawn, dehydrated with calcium chloride and re-distilled.

The operation is performed on an industrial scale in large iron pans surrounded by an outer jacket, through which cold water percolates. The pans are furnished with mechanical stirrers, which keep the acid and benzene well mixed. After the proper

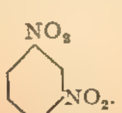
quantity of acid has been introduced and no further heat is evolved, the mixture is left to settle. The acid, which consists of diluted sulphuric acid, is withdrawn. The nitrobenzene is purified by shaking with caustic soda and water as described above. It is then ready for the next operation, or, if necessary, it is purified by distillation in a current of steam (p. 417). Nitrobenzene is a pale yellow liquid, which boils at 205° and has a specific gravity of 1·2 at 20°. It has a pleasant smell resembling that of bitter almonds, and is used under the name of *artificial oil of bitter almonds, or essence of mirbane,* for scenting cheap soap. Its chief industrial use is in the manufacture of aniline (p. 422) and benzidine (p. 442). It is poisonous.

Meta-dinitrobenzene, $C_6H_4(NO_2)_2$, is prepared by the action of a mixture of fuming nitric and strong sulphuric acids on nitrobenzene—

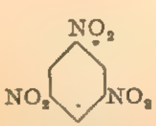
$$C_6H_5NO_2 + HNO_3 = \underset{\text{Dinitrobenzene.}}{C_6H_4(NO_2)_2} + H_2O.$$

When the acid has been added, the mixture is heated on the water-bath for a time, and then poured into water. The dinitrobenzene solidifies, and is separated from the acid by filtration, and then recrystallised from alcohol. It crystallises in long, colourless needles, melting at 90°. Dinitrobenzene is manufactured on a large scale for the preparation of certain colouring matters, and is also used as one of the ingredients of flameless explosives. *m*-Dinitrobenzene is the main product of the above reaction, but small quantities of the isomeric *o*- and *p*-dinitro-compounds are produced at the same time, and remain in the mother liquors on recrystallisation.

Trinitrobenzene, $C_6H_3(NO_2)_3$, is the product of further nitration, and has the nitro-groups in the 1-3-5-positions. It is known as *symmetrical* trinitrobenzene. Like dinitrobenzene and certain other nitro-derivatives (chlorodinitrobenzene) it is used for producing explosives for mines.

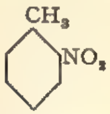


Dinitrobenzene.



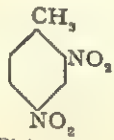
Trinitrobenzene.

Ortho- and Para-nitrotoluene, $C_6H_4(CH_3)NO_2$.—The *o*- and *p*-nitrotoluenes are produced simultaneously in almost equal quantities by the same process by which nitrobenzene is prepared. The two isomers may be partially separated by freezing. The para-compound is a solid, and melts at 54°, whereas the ortho-compound is a liquid at the ordinary temperature, and boils at 223°. The meta-compound cannot be obtained by the nitration of toluene, but has to be prepared by an indirect method which will be described later (p. 436). *Dinitrotoluene*, $C_6H_3 \cdot CH_3(NO_2)_2$, obtained by the further nitration of the mononitro-compounds, contains the nitro groups in the positions 2–4 to the methyl group. In *trinitrotoluene* the position of the nitro-groups is 2-4-6. It is a powerful shell explosive known as T.N.T. Mixed with ammonium nitrate it is known as *amatol*.



Ortho-nitrotoluene. (2.)

Para-nitrotoluene. (4.)



Dinitrotoluene. (2-4.)

2-4-6-*Trinitro-tertiary-butyl-toluene*, $C_6H(CH_3)(C_4H_9)(NO_2)_3$, has a strong smell of musk, and is manufactured as a substitute for the natural scent. A greatly superior artificial musk is, however, a cyclic ketone with an unusually large ring structure (muscone).

Positions taken by the Groups entering the Nucleus.—If reference is made to p. 408, it will be seen that, in chlorination or bromination, the halogen enters the para- and ortho-positions to the halogen or methyl group, already present in the nucleus. In the foregoing examples of nitration a difference will be apparent. The second nitro-group appropriates the meta-position to the first, although in the case of toluene it enters the ortho- and para-position to the methyl group.

It is clear, therefore, that the different groups already present in the nucleus exert a directing influence on those which are subsequently introduced. Experience has shown that certain empiric rules may be formulated, which determine the relative positions taken by chlorine, bromine, the nitro and sulphonic (SO_3H) groups on entering the nucleus.

Para-compounds, associated with varying quantities of ortho-compounds, are formed when one of the following elements, or groups, is already present in the nucleus—

$$Cl, Br, I, NH_2, OH, CH_3.$$

Meta-compounds are the main products when one of the following groups is present—

$$NO_2, COOH, SO_3H, CHO, CO{\cdot}CH_3, CN.$$

A characteristic feature of the second series is the presence of doubly-linked oxygen, or trebly-linked nitrogen, which is absent from those of the first series.

In spite of many attempts to discover the reason for this behaviour, no completely satisfactory solution has yet been found. For the present it must suffice to accept the empirical statement that the position taken by any *second* substituent depends upon the *nature of the first*, which appears to exert a definite directive influence.

Properties of the Nitro-Compounds.—A few of the nitro-compounds are liquids, but the majority are solids. The nitro-derivatives of the hydrocarbons are either colourless or yellow. Other nitro-compounds, containing hydroxyl or amino-groups in the nucleus, are frequently orange or red. They are specifically heavier than water, in which they are insoluble. Some of them may be distilled over a flame or in a current of steam; but others decompose on heating, occasionally with explosion. The nitro-compounds resemble the nitro-paraffins in their behaviour with alkalis and with reducing agents, inasmuch as they are not hydrolysed by alkalis, and, on reduction, form amino-compounds or amines. They are therefore true nitro-compounds and not nitrites. It should be remembered that the real analogues of the aromatic nitro-compounds among the nitro-paraffins are not substances like nitromethane and ethane (which dissolve and form salts with alkalis and react with nitrous acid), but the tertiary nitro-paraffins (p. 194).

The true representative of nitromethane among the aromatic compounds is *phenylnitromethane*, $C_6H_5{\cdot}CH_2{\cdot}NO_2$, which is prepared from benzyl bromide and silver nitrite—

$$C_6H_5CH_2\boxed{Br + Ag}NO_2 = \underset{\text{Phenylnitromethane.}}{C_6H_5CH_2NO_2} + AgBr.$$

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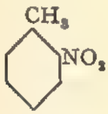

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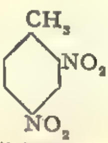

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$$C_6H_5CH_2\boxed{Br + Ag}NO_2 = \underset{\text{Phenylnitromethane.}}{C_6H_5CH_2NO_2} + AgBr.$$

The Reduction of Nitro-Compounds.—The reduction of nitro-compounds is a reaction of the greatest importance, as it offers the simplest and readiest method for obtaining aromatic amino-compounds. Nitrobenzene yields aminobenzene or aniline—

$$C_6H_5NO_2 + 3H_2 = \underset{\text{Aniline.}}{C_6H_5NH_2} + 2H_2O$$

Different reducing agents are employed for this purpose; but usually a combination of metal and acid capable of evolving hydrogen (p. 52).

EXPT. 142.—Pour a few drops of nitrobenzene into a test-tube, and add a few c.c. of glacial acetic acid and then a little zinc dust from the point of a knife. When the first reaction is over, warm gently for a minute, add a little water, and decant the clear liquid. The solution contains aniline acetate together with zinc acetate—

$$C_6H_5NO_2 + 3Zn + 7C_2H_4O_2$$
$$= \underset{\text{Aniline acetate.}}{C_6H_5NH_2{\cdot}C_2H_4O_2} + 3Zn(C_2H_3O_2)_2 + 2H_2O.$$

Add caustic soda to the solution until the zinc hydroxide redissolves, and pour the liquid, which now contains free aniline, into a solution of sodium hypochlorite. The violet colour, which is developed, is characteristic of aniline.

A somewhat different result is obtained if the reduction occurs in a neutral solution, *e.g.* by the action of zinc dust, or the aluminium-mercury couple, and water. Nitrobenzene is converted into *phenylhydroxylamine*,

$$C_6H_5NO_2 + 2H_2 = \underset{\text{Phenylhydroxylamine.}}{C_6H_5NH(OH)} + H_2O.$$

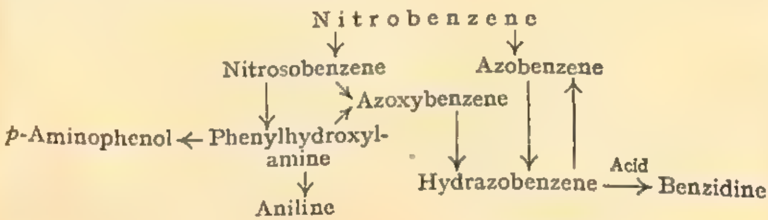
This compound doubtless forms an intermediate stage in the production of aniline. Phenylhydroxylamine is a very reactive substance; on reduction it yields aniline, and on oxidation it is first converted into *nitrosobenzene*, C_6H_5NO, and then into nitrobenzene. Nitrosobenzene is a yellow, crystalline substance, which on heating changes to an emerald-green liquid. With mineral acids, phenylhydroxylamine undergoes isomeric change to *p*-aminophenol (p. 415). It reduces Fehling's solution, and also separates iodine from potassium iodide and dilute sulphuric acid.

A totally different effect is produced by the action of alkaline reducing agents (p. 53), such as sodium methylate, zinc dust, and

caustic soda, or stannous chloride and caustic soda. Azoxy-, azo-, and hydrazo-compounds are formed. Nitrobenzene is converted in successive steps into azoxybenzene, azobenzene, and hydrazobenzene (p. 442).

$C_6H_5NO_2$	$C_6H_5N{:}O$	C_6H_5N	C_6H_5NH
	$\Vert$	$\Vert$	$\vert$
$C_6H_5NO_2$	C_6H_5N	C_6H_5N	C_6H_5NH
Nitrobenzene.	Azoxybenzene.	Azobenzene.	Hydrazobenzene.

The reduction of nitrobenzene has been effected at the cathodes of electrolytic cells. By varying the conditions different products are formed. If the acid is too concentrated, some of the phenylhydroxylamine undergoes rearrangement to the isomeric *p*-aminophenol, $HO{\cdot}C_6H_4{\cdot}NH_2$. The action of acid on hydrazobenzene is to form the isomeric compound benzidine, $H_2N{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$ (p. 442). Both changes are irreversible. In alkaline solution the main products are azobenzene and hydrazobenzene, the latter being easily oxidised again to azobenzene. The following scheme shows how the reduction goes :—



Acid Reduction. Alkaline Reduction.

Questions on Chapter XXVII

1. Write a precise account of the method of preparing and purifying nitrobenzene, in order to obtain a specimen of the pure substance.

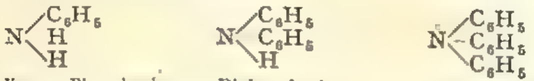
2. Describe the course of the reaction in the nitration of benzene and toluene, and the structure of the products obtained. What empiric rule may be deduced from these reactions?

3. Discuss the general laws of substitution. What products will predominate in the following reactions: (1) nitration of chlorobenzene, (2) chlorination of nitrobenzene, (3) chlorination of aniline, (4) nitration of aniline, (5) nitration of benzene sulphonic acid?

4. Compare and contrast the properties of the nitro-paraffins with the aromatic nitro-compounds.

5. What products can be obtained by the reduction of nitrobenzene and by what methods?

or an aromatic radical like phenyl—



Aniline, or Phenylamine. Diphenylamine. Triphenylamine.

The formation of these substances, many of which are of great commercial importance, is described in detail below (p. 428).

Distinction between Primary, Secondary, and Tertiary Amino-compounds.—The same reagents may be employed for distinguishing the three classes of amino-compounds as are used for the aliphatic amines, with similar, though not identical, results (p. 202).

If a solution of nitrous acid is added to a primary amino-compound and the liquid is warmed, effervescence occurs, and the amino-group is replaced by hydroxyl. Aniline yields hydroxybenzene, or ordinary phenol—

$$C_6H_5NH_2 + HNO_2 = \underset{\text{Phenol.}}{C_6H_5(OH)} + N_2 + H_2O.$$

The process actually takes place in two steps, as will be seen from the following experiment.

EXPT. 144.—Dissolve a few drops of aniline in excess of dilute hydrochloric acid (test with methyl-violet paper), cool the solution, and add a few drops of sodium nitrite solution. The liquid turns yellow, but no effervescence occurs. There is present benzene diazonium chloride (Chap. XXIX), which is very soluble in water—

$$C_6H_5NH_2{\cdot}HCl + HNO_2 = \underset{\substack{\text{Benzene diazonium}\\\text{chloride.}}}{C_6H_5N_2{\cdot}Cl} + 2H_2O.$$

Divide the liquid into two parts, and warm one portion. Effervescence occurs and nitrogen is evolved. The smell of phenol, or carbolic acid, is then perceived—

$$C_6H_5N_2Cl + H_2O = \underset{\text{Phenol.}}{C_6H_5(OH)} + N_2 + HCl.$$

Pour the other portion into a solution of phenol in caustic soda. A deep orange-red colour is at once produced. This is an *azo-colour*, the structure and properties of which will be described later (p. 443). The two reactions serve to identify a primary aromatic amino-compound.

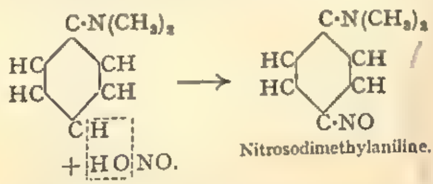
If nitrous acid is added to a secondary base, a nitrosamine is

formed, which is a yellow substance, insoluble in water. Methylaniline yields nitrosomethylaniline—

$$C_6H_5NH(CH_3) + HNO_2 = \underset{\text{Nitrosomethylaniline.}}{C_6H_5N(NO)CH_3} + H_2O.$$

EXPT. 145.—Dissolve a few drops of methylaniline in dilute hydrochloric acid, and add sodium nitrite solution as above. A precipitate consisting of fine drops of nitrosomethylaniline is formed, which may be removed by extraction with ether. It possesses a fragrant smell and yellow colour. If a few crystals of phenol are dissolved in strong sulphuric acid (2 c.c.) and a drop of nitrosomethylaniline is added, a blue colour is developed on warming, which changes to red on dilution with water. This reaction for "nitroso"-compounds is known as *Liebermann's nitroso-reaction.* Together, the above two reactions serve to identify a secondary amino-compound.

In their behaviour with nitrous acid, the tertiary amino-compounds offer no analogy with the tertiary aliphatic amines. When nitrous acid is added to dimethylaniline, a deep red solution is obtained, from which yellow crystals separate. This is the hydrochloride of a new base, nitrosodimethylaniline. The nitrous acid, here, attacks the nucleus—



Nitrosodimethylaniline.

EXPT. 146.—Dissolve a few drops of dimethylaniline in dilute hydrochloric acid. Notice that it is necessary to shake the mixture before a clear solution is obtained. Cool the liquid, and add cautiously a solution of sodium nitrite. Yellow crystals of the hydrochloride of the nitroso-compound soon begin to separate. If a portion of the liquid is made alkaline with caustic soda, a bright green precipitate is formed, which is the nitrosodimethylaniline base.

Tertiary aromatic bases, like the aliphatic tertiary amines, combine with alkyl iodides and form quaternary ammonium iodides (p. 204). Dimethylaniline, when warmed for a minute with methyl iodide, forms a crystalline trimethylphenylammonium iodide—

$$C_6H_5N(CH_3)_2 + CH_3I = \underset{\substack{\text{Trimethylphenyl-}\\ \text{ammonium iodide.}}}{C_6H_5N(CH_3)_3I.}$$

The primary and secondary bases do not yield compounds of this character.

Acetyl chloride, or acetic anhydride, may be used for distinguishing the primary and secondary from the tertiary bases. The primary and secondary amino-compounds form acetyl derivatives, but not the tertiary base.

Aniline and methylaniline give respectively acetanilide and methyl acetanilide—

$$C_6H_5NH_2 + CH_3{\cdot}COCl = \underset{\text{Acetanilide.}}{C_6H_5NH{\cdot}COCH_3} + HCl.$$

$$C_6H_5NH(CH_3) + CH_3{\cdot}COCl = \underset{\text{Methylacetanilide.}}{C_6H_5N(CH_3)CO{\cdot}CH_3} + HCl.$$

Expt. 147.—Add a few drops of acetyl chloride or acetic anhydride separately to aniline, methylaniline, and dimethylaniline. Warm for a minute over a small flame and pour into water. In the case of aniline and methylaniline, solid crystalline precipitates will be formed on rubbing with a glass rod, which are the acetyl derivatives of the two bases; but dimethylaniline is unchanged and remains liquid.

The primary aromatic amines are further distinguished by the carbamine reaction, which is described on p. 91, and also by their behaviour with carbon bisulphide. If aniline is boiled with carbon bisulphide, diluted with alcohol in a flask provided with an inverted condenser hydrogen sulphide is evolved, and a colourless, crystalline substance known as thiocarbanilide is formed—

$$SC\boxed{S + \begin{matrix} H \\ H \end{matrix}}\begin{matrix} NH{\cdot}C_6H_5 \\ NH{\cdot}C_6H_5 \end{matrix} = \underset{\text{Thiocarbanilide.}}{SC\begin{matrix} \diagup NH{\cdot}C_6H_5 \\ \diagdown NH{\cdot}C_6H_5 \end{matrix}} + H_2S.$$

Aniline, *Aminobenzene, Phenylamine,* $C_6H_5NH_2$.—Aniline was discovered in 1826 by Unverdorben among the products of the distillation of indigo. Later, Fritsche obtained it from the same source by distilling with strong potash, and called it *aniline,* from the Portuguese word *anil,* indigo. It was found in coal-tar by Runge, who discovered the reaction with hypochlorites, and named it *kyanol.* Its production from nitrobenzene by reduction is due to Zinin. Since the discovery of the aniline dyes, its manufacture has attained very large dimensions. It is prepared by the reduction of nitrobenzene with tin and hydrochloric acid as already described

(p. 416); but on the industrial scale the reducing agent is iron borings and strong hydrochloric acid. The nitrobenzene and a little hydrochloric acid are heated by means of steam in an iron pan, which is provided with a condenser, so that the escaping vapours may be either returned to the pan, or, when required, conducted to a receiver. Iron borings are added to the mixture of nitrobenzene and hydrochloric acid, which is kept in agitation by a revolving stirrer. The action, once started, continues without the application of heat until the reduction is complete. Lime is then added to neutralise the acid, and the aniline is removed by distillation with steam.

As the amount of acid employed is about $\frac{1}{40}$ of the theoretical quantity required by the equation $Fe + 2HCl = FeCl_2 + H_2$, the main reaction is probably represented as follows—

$$C_6H_5{\cdot}NO_2 + 2Fe + 4H_2O = C_6H_5{\cdot}NH_2 + 2Fe(OH)_3.$$

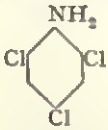
Freshly distilled aniline is a colourless, oily liquid, which rapidly darkens on exposure to light and air. It boils at 182°–183° and solidifies at $-8°$. Its specific gravity is 1·024 at 16°, and, being sparingly soluble, it sinks when poured into water. The salts of aniline have already been mentioned (p. 419). They are prepared by dissolving aniline in the respective acids, which, in the case of nitric and sulphuric acids, must be diluted. The mixture is then allowed to cool, when the salts crystallise. They become discoloured after a time if exposed to the air. The term *aniline salt* is applied technically to the hydrochloride.

Reactions of Aniline.—The presence of aniline is readily detected by pouring a drop of the base into a solution of bleaching powder or sodium hypochlorite. An intense violet coloration is produced, which slowly turns brown and fades. Another test for aniline is as follows: A few drops of strong sulphuric acid are added to a drop of aniline in a basin, and the pasty mass is stirred with a glass rod. On the addition of a few drops of potassium dichromate solution, an intense blue colour is produced.

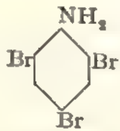
When aniline is oxidised with a cold solution of potassium dichromate and dilute sulphuric acid, it turns black, and the solution contains, among other products, *benzoquinone*, $C_6H_4O_2$, which is described later (p. 481).

Aniline undergoes the following reactions with the acids and halogens.

Chlorine and bromine act vigorously on aniline and form the 2-4-6-trichlor- and tribromaniline—



Trichloraniline.



Tribromaniline.

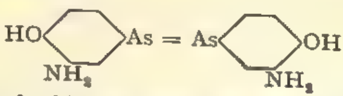
Expt. 148.—Dissolve 1 c.c. of aniline in dilute hydrochloric acid and add bromine water. A precipitate of tribromaniline is formed.

When aniline, or aniline sulphate, is heated with strong sulphuric acid, aniline *p*-sulphonic acid or sulphanilic acid is formed—

$$C_6H_5NH_2 + H_2SO_4 = C_6H_4\begin{matrix} \diagup NH_2 \\ \diagdown SO_3H \end{matrix} + H_2O.$$

Sulphanilic acid.

When aniline arsenate is heated, *p*-aminophenylarsenic acid or arsanilic acid, $H_2N{\cdot}C_6H_4{\cdot}AsO_3H_2$, is formed, the sodium salt of which has been used under the name of *atoxyl* as a specific against sleeping sickness. Its acetyl derivative or *arsacetin* is also used. By reduction of *p*-hydroxy-*m*-aminophenylarsenic acid, *a*-diamino-dihydroxy-arsenobenzene is obtained—



the hydrochloride of which is known as *salvarsan* or *arsphenamine*, and is a still more effective drug. A variety of similar arsenic compounds has been introduced into pharmacy.

The action of nitric acid on aniline is sufficiently vigorous to decompose the substance completely, unless the amino-group is "protected" by introducing an acid radical (see below).

On boiling aniline with glacial acetic acid, acetanilide is formed—

$$C_6H_5NH_2 + C_2H_4O_2 = C_6H_5NH{\cdot}C_2H_3O + H_2O.$$

Acetanilide.

Acetanilide, *Phenylacetamide, Antifebrin*, $C_6H_5NH{\cdot}C_2H_3O$, is obtained, as already mentioned, by the action of acetyl chloride, or acetic anhydride, on aniline, but is more economically prepared by boiling aniline with glacial acetic acid.

EXPT. 149.—Mix 5 c.c. of aniline with 10 c.c. of glacial acetic acid in a flask provided with a straight, upright tube about 2 feet long to condense the acetic vapour which is given off. Boil gently for about an hour and pour the contents into water. The acetanilide is precipitated as a crystalline mass, which may be purified by recrystallisation from water.

The anilides of other acids are prepared in a similar way, of which the following are examples—

Formanilide	$C_6H_5NH{\cdot}CHO$
Propionanilide	$C_6H_5NH{\cdot}CO{\cdot}C_2H_5$
Oxanilide	$C_6H_5NH{\cdot}CO{\cdot}CO{\cdot}NHC_6H_5$.

Acetanilide serves as the type of an acyl derivative of an aromatic amino-compound. It crystallises from water or dilute alcohol, and melts at 114°. It is used in medicine as a febrifuge under the name of *antifebrin*. When boiled with a strong solution of caustic alkalis, or with strong hydrochloric acid, or with moderately strong sulphuric acid, it is hydrolysed and converted into aniline and acetic acid, a reaction which recalls the behaviour of acetamide (p. 180)—

$$\begin{array}{r}C_6H_5NH\,\vdots\,CO{\cdot}CH_3\\ +\;H\,\vdots\,OH\end{array} = C_6H_5NH_2 + CH_3{\cdot}COOH.$$

EXPT. 150.—Boil 0·5 gram of acetanilide with a few c.c. of strong hydrochloric acid for a minute, and pour into water. A clear solution containing aniline hydrochloride is obtained, from which the aniline may be separated by adding caustic soda and extracting with ether in the usual way.

Nitranilines.—When acetanilide is added gradually to well-cooled, fuming nitric acid, a mixture of *o*- and *p*-nitracetanilide is produced. The nitracetanilides are precipitated by pouring the mixture into water, and after being filtered, washed, and dried, they can be separated with chloroform, which dissolves the ortho- but not the para-compound. From each of these, on hydrolysis, the corresponding nitraniline is obtained. The hydrolysis is performed, as described in Expt. 150, by boiling with strong hydrochloric acid. The product is then poured into water, made alkaline with soda (or ammonia), and the solid nitraniline filtered. The meta-com-

pound is most readily prepared by the partial reduction of *m*-dinitrobenzene with alcoholic ammonium sulphide (p. 418). It is an interesting fact that if aniline is nitrated in strong sulphuric acid solution, the chief product is *m*-nitraniline, and not the ortho- or para-compounds. The same influence of sulphuric acid has been observed in other cases (see below).

The three nitranilines are yellow, crystalline substances, which differ considerably in their melting-points. The para-compound has a technical value, being used for producing a brilliant red dye, known as *paranitraniline red* (see p. 444). Each nitraniline yields the corresponding diamino-compound, or *phenylenediamine*, $C_6H_4(NH_2)_2$, on reduction (the phenylene radical is C_6H_4''). *Tetranitraniline*, $(NO_2)_4C_6H(NH_2)$, is a powerful explosive, and so also is tetranitro-methylaniline or *tetryl*, $(NO_2)_3C_6H_4N(CH_3)NO_2$.

m-*Phenylenediamine* is usually prepared directly by the reduction of *m*-dinitrobenzene, and is employed commercially in the production of a brown colouring matter, known as *Bismarck brown* (p. 444).

		Melting-point.
$C_6H_4\langle{}^{NH_2}_{NO_2}$	*o*-nitraniline	71°
	m- ,,	114°
	p- ,,	147°
$C_6H_4\langle{}^{NH_2}_{NH_2}$	*o*-phenylenediamine	103°
	m- ,,	63°
	p- ,,	140°

Chloranilines.—If chlorine is passed into acetanilide dissolved in acetic acid, or bromine is added to the same solution, a mixture of *o*- and *p*-monochlor- or monobrom-acetanilide is first formed. If the operation is continued, these pass into the 2-4 ($NH_2 = 1$) disubstitution products. If the aniline is dissolved in strong sulphuric acid, the chlorine, or bromine, enters the meta-position to the amino-group.

A recent study of these reactions shows that when acetanilide is chlorinated or brominated by hypochlorous or hypobromous acid, chlorine and bromine first replace the hydrogen of the amino-group, from which, by intramolecular exchange, the chlorine, or bromine, enters the ortho- and para-position of the nucleus.

$$C_6H_5NH{\cdot}C_2H_3O + HClO = \underset{\text{Acetchloranilide.}}{C_6H_5NCl{\cdot}C_2H_3O} + H_2O.$$

$$C_6H_5NCl{\cdot}C_2H_3O = \underset{o\text{- and }p\text{-Chloracetanilide.}}{C_6H_4Cl{\cdot}NH{\cdot}C_2H_3O}.$$

A similar thing occurs with nitric acid. If nitrogen pentoxide is added to well-cooled aniline, the compound which is formed is phenylnitramine, and the nitro-group replaces hydrogen of the amino-group.

$$C_6H_5NH_2 + N_2O_5 = \underset{\text{Phenylnitramine.}}{C_6H_5NH{\cdot}NO_2} + HNO_3.$$

From this position, in the presence of mineral acids, the nitro-group passes into the ortho- and para-positions of the nucleus.

Alkylanilines are obtained by the action of the alkyl halide on aniline. If methyl chloride is passed into aniline, heated under pressure, methyl and dimethylaniline are formed—

$$C_6H_5NH_2 + CH_3Cl = \underset{\text{Methylaniline.}}{C_6H_5NH(CH_3)} + HCl.$$

$$C_6H_3NH(CH_3) + CH_3Cl = \underset{\text{Dimethylaniline.}}{C_6H_5N(CH_3)_2} + HCl.$$

A similar reaction occurs if the aniline is boiled with methyl bromide or iodide. The manufacturing process is to heat aniline hydrochloride or sulphate with the alcohol to 180°–200° in closed vessels.

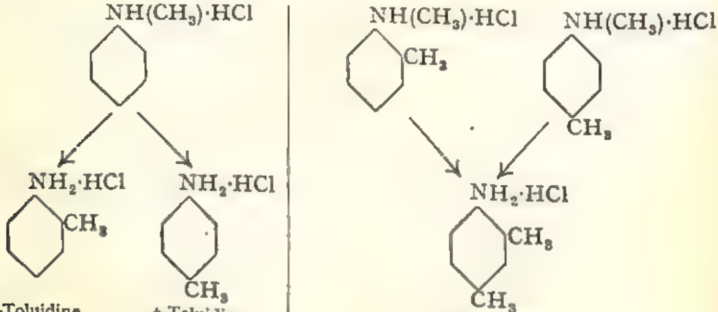
If methyl alcohol is used, it is converted into methyl chloride, or methyl sulphate (if the sulphate of aniline is used), which then acts upon the aniline.

1. $C_6H_5NH_2{\cdot}HCl + CH_3OH = C_6H_5NH_2 + CH_3Cl + H_2O.$
2. $C_6H_5NH_2 + CH_3Cl = \underset{\text{Methylaniline hydrochloride.}}{C_6H_5NHCH_3{\cdot}HCl.}$
3. $C_6H_5NH(CH_3)HCl + CH_3OH = \underset{\text{Dimethylaniline hydrochloride.}}{C_6H_5N(CH_3)_2{\cdot}HCl} + H_2O.$

In this reaction, as in Hofmann's method for preparing the aliphatic amines, both secondary and tertiary bases are formed. The separation of the tertiary base, which has the greater technical value, is effected by converting the primary and secondary bases present into acyl derivatives. For example, by boiling the mixture with acetyl chloride, or acetic anhydride, acetyl derivatives of aniline and methylaniline are formed, which have a sufficiently high boiling-point to permit of the unchanged dimethylaniline being removed by distillation.

The alkyl anilines undergo a curious intramolecular change on heating, whereby the alkyl group leaves the amino-group to enter the nucleus. The process resembles in some respects the transference of the halogens and nitro-group from the amino-group to the

nucleus (p. 426). When the hydrochloride of methyl, or dimethylaniline, is heated in closed vessels to 250°–350°, toluidine (aminotoluene) and 2-4-xylidine (aminoxylene) are formed, the methyl group entering the ortho- or para-position, or both, to the amino-group.



o-Toluidine. *p*-Toluidine. 2-4-Xylidine.

This process is of great technical importance, and is used in the manufacture of xylidine.

The alkylanilines are oily liquids, which can be distilled without decomposition. They possess a smell which recalls that of aniline with something of the fishy odour of methylamine.

Methylaniline, $C_6H_5NH(CH_3)$, is a colourless liquid of sp. gr. 0·976, which boils at 193°. It is prepared by the method described above. In this process it is separated from the dimethylaniline by conversion into the acetyl derivative, and remains when the dimethylaniline is distilled off. In order to regain the methylaniline the acetyl derivative is hydrolysed with caustic potash and the base separated and distilled. The acetyl derivative is occasionally used as a febrifuge under the name of *exalgine.*

Dimethylaniline, $C_6H_5N(CH_3)_2$, has the same boiling-point as monomethylaniline, but is readily distinguished from it by its behaviour with acetic anhydride, nitrous acid, or methyl iodide (p. 421). Dimethylanililine is manufactured on a commercial scale for the production of a variety of colouring matters, some of which will be described later.

Nitrosodimethylaniline, $(NO)C_6H_4N(CH_3)_2$, the preparation of which has already been described, is also employed in the colour industry. *Methylene-blue* is prepared from this compound.

EXPT. 151.—Warm a very small quantity of nitrosodimethylaniline with a few c.c. of ammonium sulphide solution until the substance dissolves. Cool and acidify with hydrochloric acid. Then add ferric chloride solution until the blue colour appears. The colour is known as methylene-blue.

When boiled with dilute caustic soda solution, nitrosodimethylaniline is decomposed into quinonoxime (*p*-nitrosophenol) and dimethylamine. In this manner pure dimethylamine can be obtained (p. 206).

$$\underset{\text{Nitrosodimethylaniline.}}{(NO)C_6H_4N(CH_3)_2} + H_2O = \underset{\text{Quinonoxime.}}{(HON){:}C_6H_4{:}O} + \underset{\text{Dimethylamine.}}{NH(CH_3)_2}.$$

The Toluidines, $CH_3{\cdot}C_6H_4{\cdot}NH_2$.—The three toluidines are prepared by the reduction of the corresponding nitrotoluenes. Ortho- and meta-toluidines are liquids which boil at 199°; para-toluidine is a solid, which melts at 43°, and boils about the same temperature as its isomers. Although the three toluidines possess the same boiling-point, the melting-points of their respective acetyl derivatives show a remarkable difference—

	Melting-point.
o-Acetotoluide	110°
m- „	63°
p- „	153°

Benzylamine, $C_6H_5{\cdot}CH_2NH_2$, is isomeric with the toluidines but offers a marked contrast to them both in its mode of preparation and in its properties.

It exhibits, in fact, a much closer relation to the aliphatic amines, and is prepared by similar methods. It is obtained by the action of ammonia on benzyl chloride (p. 407)—

$$C_6H_5CH_2Cl + NH_3 = \underset{\text{Benzylamine.}}{C_6H_5CH_2NH_2} + HCl.$$

Also by the action of bromine and caustic potash on the amide of phenylacetic acid, or benzyl formamide—

$$\underset{\text{Benzyl formamide.}}{C_6H_5{\cdot}CH_2{\cdot}CONH_2} + Br_2 + 4KOH$$
$$= C_6H_5\,CH_2NH_2 + 2KBr + 2H_2O + K_2CO_3.$$

It is further obtained by the reduction of phenyl cyanide—

$$\underset{\text{Phenyl cyanide.}}{C_6H_5CN} + 2H_2 = C_6H_5{\cdot}CH_2NH_2.$$

Benzylamine is an alkaline liquid, which boils at 185°, and possesses an ammoniacal smell and strongly basic properties. It behaves like a primary amine of the aliphatic series towards nitrous acid, giving the nitrite, which, on boiling with water, immediately forms the alcohol without the production of a diazo-compound—

$$C_6H_5{\cdot}CH_2NH_2{\cdot}HNO_2 = C_6H_5CH_2(OH) + N_2 + H_2O.$$

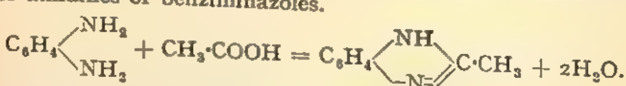
Diphenylamine, $(C_6H_5)_2NH$, is prepared by heating aniline hydrochloride and aniline to about 240° in a closed vessel—

$$C_6H_5NH_2{\cdot}HCl + C_6H_5NH_2 = \underset{\text{Diphenylamine.}}{(C_6H_5)_2NH} + NH_4Cl.$$

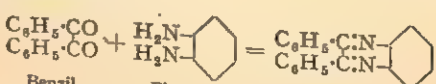
It is a colourless, crystalline compound, with a faint and not unpleasant smell. It melts at 54° and boils at 310°. The salts are decomposed by water, and the base, being insoluble, does not dissolve in dilute acids. Diphenylamine is employed in the manufacture of certain blue colouring matters. It is occasionally used to detect the presence of nitrous acid.

EXPT. 152.—Dissolve a crystal of diphenylamine in a few c.c. of strong sulphuric acid, and add a single drop of a dilute solution of a nitrite. On warming gently, a blue colour is developed.

Diamino-compounds or Diamines.—The reduction products of the three dinitrobenzenes are known as phenylenediamines (p. 426). Each of the isomers is characterised by certain properties which distinguish it from the others, and which depend upon the relative positions of the two amino-groups. These properties are shared by other diamines. The ortho-diamines, from the proximity of the two amino-groups, readily undergo condensation. With acetic acid they form so-called *anhydro-bases* or amidines or benziminazoles.



o-Phenylenediamine reacts with 1 : 2-diketones—*i.e.*, compounds containing the grouping –CO·CO–, such as benzil (p. 477) or phenanthraquinone (p. 559)—in the presence of acetic acid to give condensation products, thus—



Benzil. *o*-Phenylene-diamine.

The meta-diamines form brown colouring matters with nitrous acid, *e.g.* *m*-phenylenediamine yields Bismarck brown (p. 444).

The para-diamines give rise to a variety of red and blue colouring matters when they are submitted to oxidation in presence of a primary amino-compound (saffranines, indamines). When oxidised alone, they are converted into quinones (p. 481).

Questions on Chapter XXVIII

1. Describe and explain the process of steam distillation. How is it applied in the preparation of aniline? What other method could be used on a small scale for separating the aniline?

2. What reagents are usually employed for reduction of nitro-compounds to amino-compounds? Illustrate their use in reference to dinitrobenzene.

3. What are the principal reactions which distinguish aniline and its homologues from ethylamine and its homologues?

4. How was aniline originally obtained? From what other sources is it procurable, and how is it now manufactured?

5. How is dimethylaniline prepared from benzene? Compare and contrast the behaviour of fatty and aromatic amines towards nitrous acid.

6. Describe the action of reagents, other than nitrous acid, on the primary, secondary, and tertiary amino-compounds.

7. What is the action of the following reagents on aniline: (1) sodium hypochlorite, (2) potassium dichromate and sulphuric acid, (3) the mineral acids, (4) the halogens?

8. What is acetanilide, how is it prepared, and for what purpose is it used? In what respects does it resemble acetamide? Describe the action of the halogens on acetanilide, and explain the probable course of these reactions.

9. How are three isomeric nitranilines obtained, and what products do they yield on reduction?

10. How are the alkylanilines obtained? Give two methods. What intramolecular changes do they undergo?

11. How is dimethylaniline separated from monomethylaniline and aniline? Why is this separation necessary? In what manner can dimethylaniline be utilised for the preparation of pure dimethylamine?

12. Contrast the isomeric amino-compounds of the formula C_7H_9N.

13. What is the structure of the three phenylenediamines, and how may they be prepared from benzene? Name some of the characteristic properties of ortho-, meta-, and para-diamines.

14. Three isomeric phenylenediamine carboxylic acids have been found to yield, on distillation with lime, the same phenylenediamine. What is the constitution of the latter, and how is it most readily obtained?

of hydrochloric acid. The separation of the hydrochloric acid is assisted by the addition of sodium acetate which forms sodium chloride and free acetic acid—

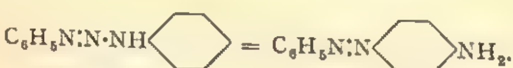
$$C_6H_5N_2\boxed{Cl + H}NHC_6H_5 = C_6H_5N{:}N{\cdot}NH{\cdot}C_6H_5 + HCl.$$

Diazoaminobenzene.

In Expt. 156 a portion of the aniline, which is present as hydrochloride, is diazotised and forms benzene diazonium chloride. The latter then unites with the free aniline, according to the equation already given.

Diazoaminobenzene crystallises from alcohol in golden-yellow plates which melt at 91°. The formation of these compounds only takes place between a diazonium salt and a primary, or secondary, but not with a tertiary amino-compound.

Aminoazobenzene, $C_6H_5N{:}N{\cdot}C_6H_4NH_2$, is formed from diazoaminobenzene by a process of intramolecular change, not unlike some examples which have already been studied (p. 428). The change consists here in the passage of the diazobenzene group from the amino-group to the nucleus, and in the para-position to the amino-group—



Diazoaminobenzene. *p*-Aminoazobenzene.

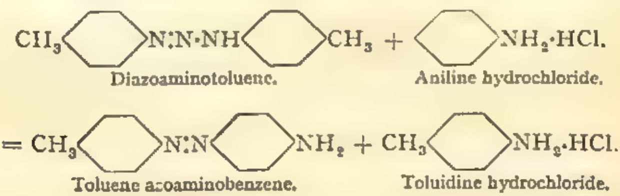
The change is brought about by dissolving the diazoaminobenzene in aniline containing a little aniline hydrochloride, and warming the mixture for a short time to 40°. The new compound is a base which forms a sparingly soluble hydrochloride. If the product of the reaction is mixed with hydrochloric acid, the aniline dissolves, and leaves the hydrochloride of aminoazobenzene in the form of minute, steel-blue needles. In order to obtain the free base, the hydrochloride is warmed with dilute ammonia. The free base has a brown colour, and was formerly used as a dye, by the name of *aniline-yellow*, but is no longer employed for this purpose. Aminoazobenzene can also be obtained from azobenzene (p. 441), which is converted into the nitro-compound and then reduced. Its structure is determined by its synthesis from azobenzene and from the products which it yields on reduction. When warmed

with tin, or stannous chloride, and hydrochloric acid, it decomposes into aniline and *p*-phenylenediamine—

$$\begin{array}{l|l} C_6H_5N{:} & NC_6H_4NH_2 \\ \quad + H_2 & H_2 \end{array} = \underset{\text{Aniline.}}{C_6H_5NH_2} + \underset{p\text{-Phenylenediamine.}}{NH_2C_6H_4NH_2}.$$

Azobenzene and other azo-compounds break up in the same fashion on reduction (p. 442).

The manner in which the conversion of diazoaminobenzene into aminoazobenzene is accomplished has not received a satisfactory explanation, but it appears that the small amount of aniline hydrochloride is the chief factor in the decomposition, and that the change is effected by the diazobenzene group leaving the amino-group of the base, to attach itself to the nucleus of the aniline hydrochloride molecule. It has been shown, in support of this view, that, on warming diazoaminotoluene with aniline hydrochloride, toluene azoaminobenzene and toluidine hydrochloride are produced—



The diazo-reaction is not entirely confined to the aromatic series. Nitrous acid acts on the ethyl esters of α-amino acids, but not on the free acids, to give aliphatic diazo-compounds, thus the ester of glycine (p. 324) gives a yellow oil, *diazoacetic ester*, $C_2H_5OOC{\cdot}CH{<}\begin{smallmatrix}N\\ \| \\ N\end{smallmatrix}$. The nitrosamine of methyl urethane (p. 337) reacts with caustic potash to give the highly poisonous yellow gas, *diazomethane*, $CH_2{<}\begin{smallmatrix}N\\ \| \\ N\end{smallmatrix}$, which is sometimes used for methylating hydroxyl groups by direct addition of the methylene group.

CHAPTER XXIX

DIAZONIUM SALTS AND DIAZO-COMPOUNDS

Diazo-compounds.—In 1860, Griess, a German chemist, discovered what is known as the **diazo-reaction,** a process of fundamental importance, not only as an aid to organic synthesis among the aromatic compounds, but as the source of a large class of synthetic dye-stuffs, known as the **azo-dyes.**

If a solution of sodium nitrite be added very slowly to an ice-cooled solution of aniline hydrochloride in hydrochloric acid, a colourless solution of *benzene diazonium chloride* is formed, which is rather unstable and decomposes unless it is used quickly—

$$\begin{array}{l} C_6H_5{\cdot}N \,\vdots\, H_2 \;\; H \,\vdots\, Cl \\ \quad + \;\; N \,\vdots\, O{\cdot}OH \,\vdots \end{array} = \underset{\substack{\text{Benzenediazonium} \\ \text{chloride.}}}{C_6H_5N_2Cl} + 2H_2O.$$

The group $C_6H_5N_2$ may be regarded as a univalent radical, derived from ammonium NH_4 by replacing one hydrogen atom by the phenyl group and three by a tervalent nitrogen atom. Like ammonium, it forms salts and an unstable hydroxide—

$$C_6H_5N_2{\cdot}Cl \qquad C_6H_5N_2{\cdot}NO_3 \qquad C_6H_5N_2{\cdot}HSO_4 \qquad C_6H_5N_2{\cdot}OH.$$

The salts when dry are very sensitive to shock, and explode on warming, and the hydroxide can be liberated as an oil, but the salts are always used in aqueous solution. The reaction is generally characteristic of primary aromatic amines.

Diazonium Salts, Diazo-compounds, and Diazotates.—The formula $C_6H_5{\cdot}N{:}N{\cdot}Cl$, which Kekulé proposed, does not satisfactorily account for the strong ionisation of these salts, and has been abandoned in favour of Blomstrand's formula,

$$\begin{array}{r@{}l} C_6H_5{\cdot}&N{\cdot}Cl \\ &\,||| \\ &N \end{array}$$

which, when amended to

$$\begin{array}{l} C_6H_5\cdot\overset{+}{N}\ \ \overset{-}{Cl} \\ \qquad\ \ ||| \\ \qquad\ \ N \end{array}$$

shows its similarity to $\overset{+}{N}H_4\overset{-}{Cl}$.

The grouping $-N{:}N-$ is, however, used for the non-ionised *diazo-compounds*, such as diazoaminobenzene (p. 437) as well as for the *azo-compounds* (p. 438), and again for an entirely different class of salts called *diazotates*. Unlike ammonium hydroxide, the diazonium bases are amphoteric, and react with caustic alkalis to give diazotates—

$$C_6H_5N_2Cl + 2NaOH = C_6H_5\cdot N{:}N\cdot ONa + NaCl + H_2O.$$

This action is reversed when excess of acid is added. The double bond between the nitrogen atoms gives rise to a kind of geometrical isomerism (p. 366). The *syn*-diazotates which are first formed being less reactive than the *anti*-diazotates, but both can be reduced to hydrazines. The *syn*-diazotates can be coupled to alkaline solutions of phenols to form azo-dyes (p. 443).

Reactions of the Diazonium Salts.—The diazonium salts can be used to give useful products either with or without the elimination of the nitrogen as gas.

1. When boiled with alcohol, effervescence due to liberated nitrogen occurs. At the same time reduction of the phenyl group to benzene takes place at the expense of the alcohol, which loses hydrogen, and is oxidised to aldehyde—

$$\begin{array}{r|c|l} C_6H_5 & N & Cl \\ & ||| & \\ + H & N & H \end{array} = C_6H_6 + N_2 + HCl.$$

An alkaline solution of sodium stannite can also be used.

2. If the aqueous solution of the diazonium chloride is boiled, nitrogen is evolved as before, and phenol is formed (p. 420)—

$$\begin{array}{r|c|l} C_6H_5 & N & Cl \\ & ||| & \\ + OH & N & H \end{array} = C_6H_5(OH) + N_2 + HCl.$$

3. When bromine, dissolved in potassium bromide, is added to a solution of the diazonium chloride, the crystalline diazobenzene perbromide is precipitated—

$$\begin{array}{l} C_6H_5N\boxed{Cl + K}Br \\ \quad \| \| \| \\ \quad N \qquad\quad + Br_2 \end{array} = \underset{\text{Diazobenzene perbromide.}}{C_6H_5NBr{\cdot}NBr_2} + KCl.$$

4. When the perbromide is boiled with alcohol, nitrogen and bromine are both given off, and bromobenzene is formed—

$$C_6H_5NBr{\cdot}NBr_2 = C_6H_5Br + N_2 + Br_2.$$

5. If a solution of potassium iodide is added to the diazonium chloride and the mixture then warmed, the usual effervescence from escaping nitrogen occurs, and iodobenzene is formed—

$$C_6H_5N_2\boxed{Cl + K}I = C_6H_5I + N_2 + KCl.$$

The **Sandmeyer reactions**, in which cuprous salts are employed, furnish a method of introducing chlorine, bromine, or the cyanogen group into the aromatic nucleus. The cuprous salts and the diazonium salts unite to form double compounds which are easily decomposed.

If the diazonium salt is added to a solution of cuprous chloride in hydrochloric acid, to cuprous bromide in hydrobromic acid, or to cuprous cyanide in potassium cyanide, the following changes occur :—

6. $$C_6H_5N_2Cl + CuCl \longrightarrow \underset{\text{Chlorobenzene.}}{C_6H_5Cl} + N_2.$$

7. $$C_6H_5N_2Cl + CuBr = \begin{array}{l} C_6H_5N_2Br \\ + CuCl \end{array} \longrightarrow \underset{\text{Bromo-benzene.}}{C_6H_5Br} + N_2.$$

8. $$C_6H_5N_2Cl + CuCN = \begin{array}{l} C_6H_5N_2CN \\ + CuCl. \end{array} \longrightarrow \underset{\text{Cyanobenzene, or Phenylcyanide.}}{C_6H_5CN} + N_2.$$

The cuprous chloride, which is formed in each case, remains in solution.

Gattermann's reaction is a modification of Sandmeyer's, finely divided copper being used in place of a cuprous salt.

All the above reactions may be carried out without isolating the diazonium salt. Even where it is necessary to replace the amino-group by hydrogen by the use of alcohol, as described in the first

reaction, the diazonium salt need not be isolated. The amino-compound is simply dissolved in alcohol and cooled, and the theoretical quantity of hydrochloric acid and powdered sodium nitrite is added. The mixture is then warmed, when effervescence occurs, and the hydrocarbon is formed.

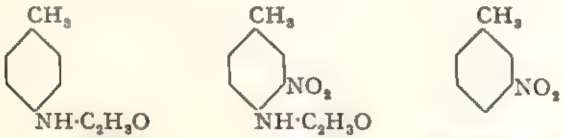
Where the product of these reactions *can* be distilled in steam, this is invariably done, especially in using Sandmeyer's reaction; for it is the only convenient way of separating the product from the copper salts. The usual method in conducting Sandmeyer's reaction is to mix the base with a slight excess of dilute acid (usually hydrochloric acid), and to add the theoretical quantity of sodium nitrite, either in the solid form or in solution, keeping the mixture well cooled in ice. The nitrite is added until the presence of free nitrous acid can be detected with potassium iodide and starch. If the iodo-compound is prepared, a solution of potassium iodide is added; if the chloro-, bromo-, or cyano-compound is required, the solution of the diazonium salt is poured into the solution of the respective cuprous salt, and the product is then distilled in steam. If the hydroxy-compound is prepared, the aqueous solution of the diazonium salt is simply warmed and then distilled in steam.

EXPT. 153. *Preparation of Benzene diazonium sulphate.*—In order to study the above reactions of the diazonium salts, it is desirable to isolate the substance itself, which can be done in the following way without incurring any risk. In order that the diazonium salt shall be precipitated, the reaction is carried out in alcoholic solution. 15 grams of aniline are mixed with 140 grams of pure ethyl alcohol, and 30 grams of strong sulphuric acid are added. The alcoholic solution of aniline sulphate is cooled to 35°, and 20 grams of amyl nitrite are then slowly added. Amyl nitrite is hydrolysed in presence of sulphuric acid, and is the source of nitrous acid. If, after the addition of amyl nitrite, the liquid is cooled in ice, a mass of colourless crystals of benzene diazonium sulphate will separate. It is filtered and washed with a little alcohol. Portions are then dissolved in alcohol, or water, and the various reagents described in the different reactions added in succession.

The results of this many-sided reaction may now be briefly summarised. The nuclear amino-group can be replaced by hydrogen, the halogens, cyanogen, and hydroxyl.

We will take one example of the synthetic uses of this reaction. It may be applied to the preparation of *m*-nitrotoluene, which

cannot be accomplished by the direct nitration of toluene (p. 412). If *p*-acetotoluidide is nitrated, the nitro-group, according to the rule, seeks the ortho- or para-position to the amino-group. The para-position, however, is occupied by the methyl group; it, therefore, enters the ortho-position to the amino-group, which is meta- to the methyl group. The compound, which is *m*-nitro-*p*-acetotoluidide, is hydrolysed, and the hydrochloride of the base diazotised in presence of alcohol. The amino-group is thus replaced by hydrogen, and *m*-nitrotoluene results—



p-Acetotoluidide. *m*-Nitro-*p*-acetotoluidide. *m*-Nitrotoluene.

From *m*-nitrotoluene, *m*-toluidine and the *m*-halogen compounds may be obtained by the diazo-reaction.

Phenylhydrazine, $C_6H_5{\cdot}NH{\cdot}NH_2$, is obtained by the reduction of benzene diazonium chloride by means of stannous chloride dissolved in hydrochloric acid—

$$C_6H_5N_2Cl + 2SnCl_2 + 4HCl = \underset{\text{Phenylhydrazine hydrochloride.}}{C_6H_5NH{\cdot}NH_2{\cdot}HCl} + 2SnCl_4.$$

The hydrochloride of phenylhydrazine is formed, from which caustic soda liberates the phenylhydrazine as an oil, which is extracted with ether. After removing the ether by distillation, the phenylhydrazine remains as a reddish oil, which may be purified by distillation under diminished pressure when it crystallises.

EXPT. 154.—Dissolve 2 grams of aniline in 10 c.c. of strong hydrochloric acid, cool well, and add 2 grams of sodium nitrite. On the addition of a solution of 12 grams of stannous chloride in 10 c.c. of strong hydrochloric acid, a thick white precipitate of phenylhydrazine hydrochloride is thrown down.

Phenylhydrazine, when freshly distilled, is a nearly colourless oil, which boils at 242° and melts at 23° C. It is a strongly basic substance with an ammoniacal smell. It forms well-crystallised

salts, which are colourless when freshly prepared; but both the base and its salts become discoloured on exposure to light and air. Its behaviour as a reagent for detecting aldehydes and ketones (p. 131) and the sugars (p. 292) has already been described. It has strong reducing properties. It precipitates cuprous oxide from Fehling's solution, nitrogen being evolved and benzene formed—

$$C_6H_5NH{\cdot}NH_2 + 2CuO = C_6H_6 + Cu_2O + H_2O + N_2.$$

The formation of benzene also occurs if phenylhydrazine acetate is warmed with copper sulphate solution.

EXPT. 155.—The reducing action of phenylhydrazine on copper oxide has been utilised in order to obtain a deposit of metallic copper on glass. Dissolve in a wide test-tube 1 part of phenylhydrazine in 2 parts of boiling water, add one-quarter the bulk of Schweitzer's reagent and hot caustic potash (50 per cent.) until there is a precipitate of cuprous oxide. Place in a beaker of hot water, when a copper mirror will form on the glass.

With zinc dust and hydrochloric acid, phenylhydrazine is decomposed into aniline and ammonia—

$$\begin{array}{l} C_6H_5NH{\cdot}\vdots NH_2 \\ \quad\; + H\vdots H \end{array} = C_6H_5NH_2 + NH_3.$$

The various derivatives of phenylhydrazine, such as the para-, bromo-, and nitro-compounds, are obtained from the corresponding aniline derivatives, and are likewise used as reagents. Phenylhydrazine is used in the manufacture of **antipyrine** (p. 567). Its acetyl derivative has also been applied as an antipyretic under the name of *pyrodin*.

Diazoaminobenzene, $C_6H_5N{:}N{\cdot}NHC_6H_5$.—If benzene diazonium chloride is added to aniline, a yellow, crystalline compound is formed, which is known as diazoaminobenzene.

EXPT. 156.—A similar result to the above is produced if a few c.c. of aniline are mixed with a little water and hydrochloric acid is added, so that some of the aniline remains undissolved. If a solution of sodium nitrite is poured into the mixture and stirred, the liquid becomes turbid, and soon deposits diazoaminobenzene in the form of a yellow, or brown, crystalline substance.

The reaction involves the condensation of a molecule of benzene diazonium chloride with a molecule of aniline and the elimination

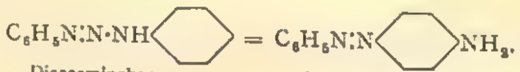
of hydrochloric acid. The separation of the hydrochloric acid is assisted by the addition of sodium acetate which forms sodium chloride and free acetic acid—

$$C_6H_5N_2\boxed{Cl + H}NHC_6H_5 = \underset{\text{Diazoaminobenzene.}}{C_6H_5N{:}N{\cdot}NH{\cdot}C_6H_5} + HCl.$$

In Expt. 156 a portion of the aniline, which is present as hydrochloride, is diazotised and forms benzene diazonium chloride. The latter then unites with the free aniline, according to the equation already given.

Diazoaminobenzene crystallises from alcohol in golden-yellow plates which melt at 91°. The formation of these compounds only takes place between a diazonium salt and a primary, or secondary, but not with a tertiary amino-compound.

Aminoazobenzene, $C_6H_5N{:}N{\cdot}C_6H_4NH_2$, is formed from diazoaminobenzene by a process of intramolecular change, not unlike some examples which have already been studied (p. 428). The change consists here in the passage of the diazobenzene group from the amino-group to the nucleus, and in the para-position to the amino-group—



Diazoaminobenzene. *p*-Aminoazobenzene.

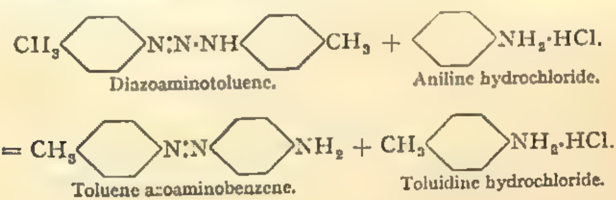
The change is brought about by dissolving the diazoaminobenzene in aniline containing a little aniline hydrochloride, and warming the mixture for a short time to 40°. The new compound is a base which forms a sparingly soluble hydrochloride. If the product of the reaction is mixed with hydrochloric acid, the aniline dissolves, and leaves the hydrochloride of aminoazobenzene in the form of minute, steel-blue needles. In order to obtain the free base, the hydrochloride is warmed with dilute ammonia. The free base has a brown colour, and was formerly used as a dye, by the name of *aniline-yellow*, but is no longer employed for this purpose. Aminoazobenzene can also be obtained from azobenzene (p. 441), which is converted into the nitro-compound and then reduced. Its structure is determined by its synthesis from azobenzene and from the products which it yields on reduction. When warmed

with tin, or stannous chloride, and hydrochloric acid, it decomposes into aniline and *p*-phenylenediamine—

$$\begin{array}{l} C_6H_5N{:}\,\vdots\,NC_6H_4NH_2 \\ \quad + H_2\,\vdots\,H_2 \end{array} = \underset{\text{Aniline.}}{C_6H_5NH_2} + \underset{p\text{-Phenylenediamine.}}{NH_2C_6H_4NH_2.}$$

Azobenzene and other azo-compounds break up in the same fashion on reduction (p. 442).

The manner in which the conversion of diazoaminobenzene into aminoazobenzene is accomplished has not received a satisfactory explanation, but it appears that the small amount of aniline hydrochloride is the chief factor in the decomposition, and that the change is effected by the diazobenzene group leaving the amino-group of the base, to attach itself to the nucleus of the aniline hydrochloride molecule. It has been shown, in support of this view, that, on warming diazoaminotoluene with aniline hydrochloride, toluene azoaminobenzene and toluidine hydrochloride are produced—



The diazo-reaction is not entirely confined to the aromatic series. Nitrous acid acts on the ethyl esters of α-amino acids, but not on the free acids, to give aliphatic diazo-compounds, thus the ester of glycine (p. 324) gives a yellow oil, *diazoacetic ester*, $C_2H_5OOC\cdot CH\!<\!\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix}$. The nitrosamine of methyl urethane (p. 337) reacts with caustic potash to give the highly poisonous yellow gas, *diazomethane*, $CH_2\!<\!\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix}$, which is sometimes used for methylating hydroxyl groups by direct addition of the methylene group.

QUESTIONS ON CHAPTER XXIX

1. What is the "diazo"-reaction? Indicate how it is applied to the preparation of hydrocarbons, phenols, nitriles (cyanides), and halogen substitution-products respectively.

2. By what process can acetylene be converted into benzene and benzene into phenol?

3. Calculate the quantity of hydrochloric acid and sodium nitrite required to convert 20 grams of aniline into phenol, and the theoretical amount of product obtainable.

4. What are Sandmeyer's reactions? Give some details of the preparation of bromobenzene from aniline by Sandmeyer's reaction. What other method, involving the diazo-reaction, may be used?

5. Describe the preparation of benzene diazonium sulphate. Explain what happens if it is dissolved in water and (1) potassium iodide, (2) bromine, (3) aniline are added.

6. How is meta-chlorotoluene obtained?

7. How is phenylhydrazine obtained? Give a brief account of the classes of compounds to which it can give rise.

8. By what reactions is aminoazobenzene prepared from benzene?

9. By what means has the structure of aminoazobenzene been ascertained?

CHAPTER XXX

THE AZO-COMPOUNDS

The Azo-compounds, including aminoazobenzene, which strictly belongs to this group, differ from the diazo-compounds by their much greater stability. This is ascribed to the fact that each of the doubly-linked nitrogen atoms is attached to a benzene nucleus. This group includes the important class of azo-colours.

Azobenzene, $C_6H_5N{:}N{\cdot}C_6H_5$, is the simplest of the azo-compounds. It is usually prepared in the laboratory by distilling *azoxybenzene* with iron filings, the former being obtained by the reduction of nitrobenzene with sodium methylate (p. 415)—

$$\underset{\text{Azoxybenzene.}}{C_6H_5\underset{\substack{\| \\ O}}{N}{:}NC_6H_5} + Fe = \underset{\text{Azobenzene.}}{C_6H_5N{:}NC_6H_5} + FeO.$$

The red distillate solidifies on cooling, and is crystallised from petroleum. Azobenzene may also be prepared directly from nitrobenzene by the action of zinc dust in presence of caustic soda, or of an alkaline solution of stannous chloride on nitrobenzene—

$$2C_6H_5NO_2 + 4H_2 = C_6H_5N{:}NC_6H_5 + 4H_2O.$$

It crystallises in brilliant red plates, which melt at 68°. Azobenzene, though not a dye, may be regarded as the parent substance of the large family of azo-colours, in the sense that the azo-colours are derivatives of azobenzene, though they are not obtained from it, and the method of preparing them is quite distinct from that of azobenzene.

When azobenzene is reduced with alcoholic ammonium sulphide,

or with zinc dust and caustic soda, in alcoholic solution, reduction to hydrazobenzene takes place—

$$C_6H_5{\cdot}N{:}N{\cdot}C_6H_5 + 2H = \underset{\text{Hydrazobenzene.}}{C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5}.$$

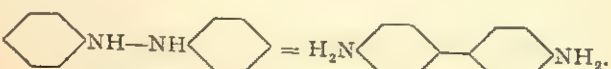
With stannous chloride and hydrochloric acid azobenzene breaks up into two molecules of aniline—

$$C_6H_5{\cdot}N{:}N{\cdot}C_6H_5 + 2H_2 = 2C_6H_5{\cdot}NH_2.$$

This reaction is characteristic of azo-compounds (p. 446).

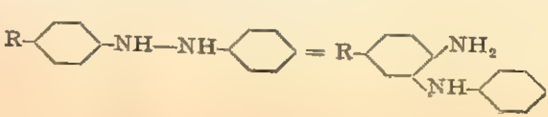
Hydrazobenzene, $C_6H_5NH{\cdot}NHC_6H_5$, is produced from azobenzene as described above, or it may be prepared directly from nitrobenzene by the addition of zinc dust to a boiling alcoholic solution of nitrobenzene containing caustic soda, until the red colour of azobenzene disappears and the liquid becomes nearly colourless. The liquid, which is filtered, deposits hydrazobenzene, on cooling, in small crystalline, colourless plates, melting at 126°. Hydrazobenzene readily oxidises and turns orange in the air, from the formation of azobenzene.

When hydrazobenzene is treated first in the cold and then warmed with hydrochloric acid, it undergoes a curious intramolecular change, which in certain respects resembles the formation of aminoazobenzene (p. 438). The product is a base known as **benzidine,** or diaminodiphenyl, and the change is sometimes called the *benzidine conversion*. It may be explained by supposing that the bond, which unites the two nitrogen atoms in hydrazobenzene, is transferred to the two nuclear carbon atoms in the para-position to the amino-groups—



Hydrazobenzene. Benzidine.

If a para-position is already substituted in hydrazobenzene a partial, so-called *semidine* conversion results—



The process is one of great technical importance, as benzidine and its homologue (tolidine) are used in the manufacture of valuable azo-colours.

EXPT. 157.—Boil a few crystals of hydrazobenzene with a little strong hydrochloric acid for a minute, dilute with a little water, filter, and add ammonia to the filtrate. Benzidine is precipitated in glistening, colourless, flaky crystals.

The Azo-colours.—This important group of dyes is obtained by adding the solution of a diazonium salt to an aromatic amino- or hydroxy-compound, or to a derivative, usually the sulphonic acid. The following experiments will illustrate the process.

EXPT. 158.—Dissolve a few drops of aniline in excess of dilute hydrochloric acid, and convert it into the diazonium salt, by adding sodium nitrite solution in the usual way.

1. Pour a portion of the liquid into a solution of dimethylaniline in hydrochloric acid. The solution contains the azo-colour, which is formed as follows—

$$C_6H_5N_2Cl + C_6H_5N(CH_3)_2 = \underset{\text{Dimethylaminoazobenzene hydrochloride.}}{C_6H_5N{:}N{\cdot}C_6H_4N(CH_3)_2{\cdot}HCl.}$$

2. Add another portion of the diazonium salt solution to ordinary phenol dissolved in caustic soda, and a third portion to β-naphthol (hydroxynaphthalene) in caustic soda.

In both cases colours (orange or red) are produced from the formation of the sodium salts of hydroxyazo-compounds—

$$C_6H_5N_2{\cdot}Cl + C_6H_5(ONa) = \underset{\text{Sodium hydroxyazobenzene.}}{C_6H_5N{:}NC_6H_4(ONa)} + HCl.$$

$$C_6H_5N_2{\cdot}Cl + C_{10}H_7(ONa) = \underset{\text{Sodium hydroxynaphthalene-azobenzene.}}{C_6H_5N{:}N{\cdot}C_{10}H_6(ONa)} + HCl.$$

3. A derivative of an amino-compound may be used as the compound to be diazotised in place of a simple base like aniline. Diazotise sulphanilic acid (aniline p-sulphonic acid) with hydrochloric acid and sodium nitrite in the same way as aniline, taking care to avoid an excess of the nitrite. Add the solution to dimethylaniline dissolved in hydrochloric acid. The red colour is the free sulphonic acid of the azo-colour. The sodium salt is precipitated in orange crystals on adding caustic soda, and is known as *methyl-orange, helianthin*, or sometimes as *tropæolin*—

$$SO_3H{\cdot}C_6H_4N_2{\cdot}Cl + C_6H_5N(CH_3)_2 = \underset{\text{Methyl-orange.}}{SO_3H{\cdot}C_6H_4N{:}N{\cdot}C_6H_4N(CH_3)_2} + HCl.$$

4. Dissolve a little *m*-phenylenediamine (p. 426), or the hydrochloride in hydrochloric acid, and add a drop of sodium nitrite solution. The brown colour, which is produced, is an azo-dye known as *Bismarck brown*. One amino-group of the diamine molecule is diazotised and unites with a second molecule of the diamine to form an azo-colour—

$$(NH_2)C_6H_4N_2{\cdot}Cl + C_6H_4(NH_2)_2 = \underset{\text{Bismarck brown.}}{(NH_2)C_6H_4N{:}N{\cdot}C_6H_3(NH_2)_2{\cdot}HCl.}$$

The formation of deeply coloured solutions, by the action of nitrous acid on organic bases, is utilised as above for detecting small quantities of nitrous acid, as in water analysis. Meta-phenylenediamine in hydrochloric acid solution becomes yellow or orange in presence of a trace of nitrite in water.

5. Diazotise aniline in the usual way, and add it to a solution of *m*-phenylenediamine. The orange colour is *chrysoidine hydrochloride*—

$$C_6H_5N{:}N{\cdot}C_6H_3(NH_2)_2{\cdot}HCl.$$

Chrysoidine, or Diaminoazobenzene hydrochloride.

6. To illustrate the formation of an azo-dye on the cloth, soak strips of cotton cloth in a solution of 1 gram of β-naphthol and 1 gram of NaOH in 100 c.c. of water and dry in the steam-oven in the dark. Make up a solution of *p*-nitraniline hydrochloride by first dissolving 1 gram of nitraniline in a mixture of 2 c.c. of conc. HCl and 2 c.c. of water and, when dissolved, diluting to 30 c.c. Diazotise the base by adding 5 c.c. of a 10 per cent. sodium nitrite solution in the cold and make up to about 100 c.c. with a 10 per cent. solution of sodium acetate. Make up a second solution with dianisidine in the same way. On dipping the strips of cloth into the diazo-solution prepared from *p*-nitraniline, a bright red colour will be developed, and in that from the anisidine a deep blue.

From these examples it will be seen that two molecules take part in the process of producing an azo-dye: on the one hand, an aromatic amino-compound, and, on the other, a base or phenol. The first is diazotised, and combined or coupled with the second. The coupling takes place in the case of amines in a faintly acid solution, in the case of phenols in an alkaline solution.

In all cases the diazo-group seizes upon the carbon in the para-position to the amino- or hydroxyl group of the coupled nucleus. When the para-position is already appropriated, the ortho-position serves as the link, but no coupling ever occurs in the meta-position. The sulphonic acid derivatives of the base or phenol are frequently preferred to the unsubstituted compound. The dyes to which they

give rise have, in consequence of the presence of the SO_3H group, an acid character, which renders them capable of forming soluble sodium salts. They are also better adapted for dyeing.

When an azo-compound is formed by coupling the diazo-compound with a primary amine, the new product is capable of being diazotised and coupled a second time. Thus, what is known as a *tetrazo-compound* is formed, containing a double diazo-group —N:N—. Aminoazobenzene, when diazotised, forms diazo-azobenzene with nitrous acid, which, like a simple diazo-compound, reacts with the phenols.

$$C_6H_5N{:}N{\cdot}C_6H_4NH_2{\cdot}HCl + HNO_2 = C_6H_5N{:}N{\cdot}C_6H_4N_2{\cdot}Cl + 2H_2O$$

$$C_6H_5N{:}N{\cdot}C_6H_4N_2{\cdot}Cl + C_6H_5OH$$
$$= C_6H_5N{:}N{\cdot}C_6H_4N{:}N{\cdot}C_6H_4(OH) + HCl.$$

If aminoazobenzene is sulphonated so as to produce a disulphonic acid, and then the product diazotised and coupled with β-naphthol, *Biebrich scarlet* is formed—

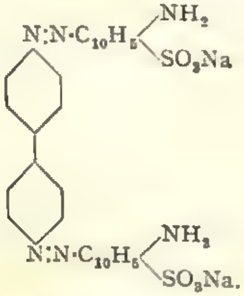
$$C_6H_4{<}^{SO_3H}_{N:N\cdot C_6H_3}{<}^{SO_3H}_{N:N\cdot C_{10}H_6(OH).}$$

Biebrich scarlet.

If, in the last phase, the different sulphonic acids of β-naphthol are employed, various shades of red, known as *Croceins*, are produced. Thus, it appears that the colour deepens from orange to red with the introduction of a second azo-group. This is not the only method of forming tetrazo-compounds. Each amino-group of a diamino-compound may be diazotised and coupled. Benzidine (diaminodiphenyl) and its homologues have been utilised in this way, and have a special value for the cotton dyer, as the shades produced are not only very brilliant, but, unlike the majority of colouring matters, are *substantive colours, i.e.* possess the property of attaching themselves to the cotton fibre without the aid of a *mordant*. With other azo-colours the fibre is first impregnated with tannin and tartar emetic, which forms insoluble antimony tannate on the fibre. This constitutes the mordant, and is capable of absorbing and fixing the colour. Colours fixed by a mordant are sometimes called *adjective colours* (see p. 521).

Congo reds and *benzopurpurins* are combinations of benzidine and its homologues with the sulphonic acids of naphthol and

naphthylamine. The following is the constitution of Congo red, the simplest of these compounds, which is used in the form of its sodium salt :—



The constitution of an azo-colour may frequently be ascertained by reduction, when cleavage takes place with the addition of hydrogen at the doubly-linked nitrogen atoms. Thus if methyl-orange is heated with a solution of stannous chloride in conc. hydrochloric acid or sodium hydrosulphite, it becomes colourless and breaks up into sulphanilic acid and dimethyl *p*-phenylene-diamine.

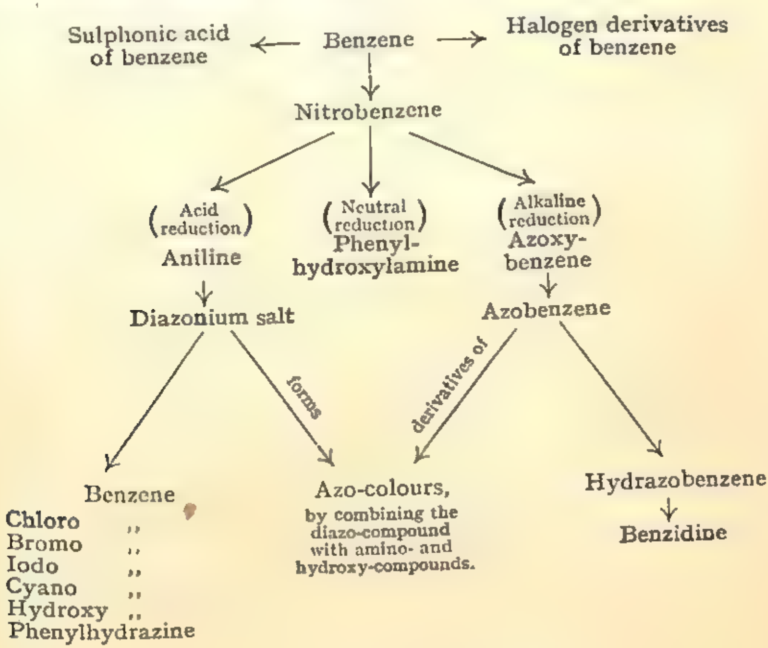
$$HO_3S{\cdot}C_6H_4N{:}N{\cdot}C_6H_4N(CH_3)_2 + 2H_2 = HO_3S{\cdot}C_6H_4NH_2 + H_2N{\cdot}C_6H_4{\cdot}N(CH_3)_2.$$

EXPT. 159.—Make a solution of 4 grams of $SnCl_2$ in 10 c.c. of conc. HCl, add 1 gram of methyl-orange dissolved in a few drops of water, and boil for a minute or two. The red colour will disappear, and, on cooling, a crystalline precipitate consisting of a mixture of sulphanilic acid and dimethyl *p*-phenylenediamine hydrochloride separates.

Attention must be drawn to the fact that azobenzene, although a brightly coloured substance, is without dyeing properties, *i.e.* it cannot be fixed as a colour upon the fibre, whereas aminoazo-benzene and methyl-orange are true dyes. They all three contain the azo-group (—N:N—), called by Witt a *chromophoric group*, united to two aromatic nuclei; but, in the case of aminoazobenzene and methyl-orange, one of these nuclei contains a basic group, NH_2 or $N(CH_3)_2$. It will also have been observed that the combinations with phenols likewise result in the production of dyes. It would appear, therefore, as if there were at least two essentials to a dye, a fundamental or parent substance like azobenzene, termed

a *chromogenic* compound, and an amino- or hydroxyl group, called an *auxochrome*. The same thing has been observed in the case of other colouring matters.

In concluding the chapters on the diazo- and azo-compounds, the following synopsis is appended in the form of a table, which gives a general view of the connection of the various groups of aromatic compounds which have been so far described. It should be remembered that many of the homologues of benzene undergo a similar series of chemical changes.



Questions on Chapter XXX

1. How do you explain the greater stability of the azo-compounds compared with the diazo-compounds?

2. How is azobenzene obtained? What products does it give on reduction? In what sense is it to be regarded as the parent substance of the azo-dyes?

3. Describe two important examples of intramolecular change used in the preparation of aromatic compounds.

4. Starting with nitrobenzene, explain how the following compounds can be prepared—(*a*) azoxybenzene, (*b*) azobenzene, (*c*) hydrazobenzene, (*d*) aniline, (*e*) phenylhydroxylamine, (*f*) benzidine.

5. What are the *azo-compounds ?* Illustrate their formation by the action of diazotised sulphanilic acid (*p*-aminobenzene sulphonic acid) on phenol.

6. What is the general constitution of the principal types of azo-dyes, known as chrysoidines, tropeolines, and Congo colours ? Indicate how they are produced and applied.

7. What explanation has been offered of the colouring properties of the azo-dyes ?

8. What mordant is used in connection with the azo-dyes ? What is meant by a *substantive* dye ? Give an example.

CHAPTER XXXI

THE SULPHONIC ACIDS

The Sulphonic Acids.—It has already been stated (p. 390) that the aromatic hydrocarbons possess the distinctive property of forming sulphonic acids, when heated with strong, or fuming, sulphuric acid. The process is called **sulphonation.** Benzene forms benzenesulphonic and disulphonic acids. In the disulphonic acid, the process of substitution follows the general rule (p. 412), and the main product is the meta-compound—

$$C_6H_6 + H_2SO_4 = \underset{\text{Benzenesulphonic acid.}}{C_6H_5{\cdot}SO_3H} + H_2O.$$

$$C_6H_5{\cdot}SO_3H + H_2SO_4 = \underset{m\text{-Benzene-disulphonic acid.}}{C_6H_4(SO_3H)_2} + H_2O.$$

Sometimes chlorosulphonic acid may be used with advantage in place of sulphuric acid—

$$C_6H_6 + \underset{\text{Chlorosulphonic acid.}}{ClSO_3H} = C_6H_5SO_3H + HCl.$$

Sulphonation is not confined to the hydrocarbons, but may be extended to their derivatives. When aniline is heated with sulphuric acid to 180°, it forms aniline *p*-sulphonic acid, or sulphanilic acid (p. 424)—

$$NH_2{\cdot}C_6H_5 + H_2SO_4 = \underset{\text{Sulphanilic acid.}}{NH_2{\cdot}C_6H_4{\cdot}SO_3H} + H_2O.$$

Chloro- and nitro- and hydroxy-derivatives of benzene behave in a similar fashion.

The preparation of benzene sulphonic acid may be taken to illustrate the process of sulphonation.

Benzenesulphonic Acid, $C_6H_5{\cdot}SO_3H$.—Benzene is heated on a sand-bath with twice its weight of strong sulphuric acid in a flask provided with an inverted condenser. The contents must be

thoroughly agitated by a stirrer so as to mix the acid and hydrocarbon. The reaction is accompanied by a considerable evolution of heat, the benzene gradually dissolving in the acid. To obtain the sodium salt of the sulphonic acid, it is customary to pour the product into a strong solution of common salt, when sodium benzenesulphonate at once crystallises and hydrochloric acid is evolved—

$$C_6H_5\cdot SO_3H + NaCl = \underset{\text{Sodium benzene-sulphonate.}}{C_6H_5SO_3Na} + HCl.$$

The calcium, barium, or lead salt is obtained by adding the carbonate of the metal to the product of sulphonation diluted with water. The carbonate precipitates the excess of sulphuric acid as sulphate of the metal, and at the same time forms a soluble sulphonate with the sulphonic acid—

$$2C_6H_5\cdot SO_3H + CaCO_3 = \underset{\text{Calcium benzene-sulphonate.}}{(C_6H_5SO_3)_2Ca} + CO_2 + H_2O.$$

The hot solution is filtered and evaporated until the point of crystallisation is reached. If the potassium salt is required, potassium carbonate is added to the solution of calcium, barium, or lead sulphonate, the insoluble carbonate of the metal removed by filtration, and the filtrate evaporated—

$$(C_6H_5SO_3)_2Ca + K_2CO_3 = \underset{\text{Potassium benzene-sulphonate.}}{2C_6H_5\cdot SO_3K} + CaCO_3.$$

Finally, if the free sulphonic acid is to be prepared, the metal in the solution of the barium or lead sulphonate is exactly precipitated with sulphuric acid, or, in the case of the lead salt, with hydrogen sulphide, and the filtrate evaporated on the water-bath—

$$(C_6H_5SO_3)_2Pb + SH_2 = 2C_6H_5\cdot SO_3H + PbS.$$

Properties of the Sulphonic Acids.—The sulphonic acids are strong acids. They redden blue litmus and form well-crystallised salts which frequently contain water of crystallisation. The free acids are very soluble in water, and are in some cases hygroscopic. The solubility of the sulphonic acids and their salts in water is a property which is often turned to advantage. Insoluble dyes have

frequently been converted into soluble substances by sulphonation (p. 521).

The sulphonic acids decompose on heating, and have therefore no definite melting-point. When heated with strong hydrochloric acid in closed tubes, or with strong sulphuric acid in a current of steam, the sulphonic acids and sulphonates are decomposed, the sulphonic group being split off and replaced by hydrogen. The process is one of hydrolysis. Benzenesulphonic acid is converted into benzene—

$$C_6H_5 \cdot SO_3H + H_2O = C_6H_6 + H_2SO_4.$$

The method is sometimes used for separating hydrocarbons one of which is more easily sulphonated than another. The sulphonic acid dissolves in the sulphuric acid, and is easily separated from the unchanged and insoluble hydrocarbon. The sulphonated hydrocarbon is then hydrolysed and the hydrocarbon recovered. Or, if both hydrocarbons are sulphonated, they may be separated by fractional crystallisation of one of the salts, and then hydrolysed. A good example of the two processes is afforded by the three xylenes, which occur together in the commercial product from coal-tar (p. 395). On shaking with strong sulphuric acid, *o*- and *m*-xylene dissolve as sulphonic acids. The para-compound is unchanged and separated. The *o*- and *m*-xylene sulphonic acids are converted into the sodium salts, and separated by fractional crystallisation. Finally, each of the sulphonates is decomposed by distillation in steam with strong sulphuric acid. In this way, the three xylenes are separated.

An important property of the alkali sulphonates is their behaviour on fusion with caustic alkalis and an alkali cyanide. In the one case, a phenol is obtained (p. 456), and, in the other, a cyanide. Sodium benzenesulphonate yields ordinary phenol in the first reaction, and phenyl cyanide in the second—

$$\underset{\substack{\text{Potassium}\\\text{benzenesulphonate.}}}{C_6H_5SO_3Na} + NaOH = \underset{\text{Phenol.}}{C_6H_5OH} + Na_2SO_3.$$

$$\underset{\substack{\text{Potassium}\\\text{benzenesulphonate.}}}{C_6H_5SO_3Na} + NaCN = \underset{\substack{\text{Phenyl}\\\text{cyanide.}}}{C_6H_5CN} + Na_2SO_3.$$

The formation of cyanides by this reaction has more of theoretical

interest than practical value, the cyanides being as a rule more easily prepared by the diazo-reaction (p. 434).

Structure of the Sulphonic Acids.—The acidic character of the sulphonic acids points to the presence of a hydroxyl group. This is confirmed by the action of phosphorus pentachloride, which yields a sulphonic chloride. Benzenesulphonic acid forms benzenesulphonic chloride, just as acetic acid forms acetyl chloride (p. 175)—

$$C_6H_5SO_3H + PCl_5 = \underset{\text{Benzene-sulphonic chloride.}}{C_6H_5SO_2Cl} + HCl + POCl_3.$$

$$CH_3\cdot CO_2H + PCl_5 = CH_3\cdot COCl + HCl + POCl_3.$$

If the sulphonic chloride is reduced with zinc dust and sulphuric acid, it forms benzenesulphinic acid, and finally phenyl mercaptan—

$$\underset{\text{Benzenesulphonic acid.}}{C_6H_5\cdot SO_2\cdot OH} \rightarrow \underset{\text{Benzenesulphinic acid.}}{C_6H_5SO\cdot OH} \rightarrow \underset{\text{Phenyl mercaptan.}}{C_6H_5SH}$$

The sulphur in the mercaptan is linked to the carbon of the radical, or nucleus. Hence, the structural formula of benzenesulphonic acid must be represented by the following formula (p. 198).

$$\begin{array}{c} C_6H_5\cdot S\cdot OH \\ \swarrow \searrow \\ O \quad O \end{array}$$

Structural formula of benzenesulphonic acid.

Benzenesulphonic Chloride, $C_6H_5\cdot SO_2Cl$.—The mode of preparation of benzenesulphonic chloride may be taken as typical for this class of compounds. Benzenesulphonic acid, or, usually, one of its salts, is heated on the water-bath with phosphorus pentachloride until the evolution of hydrogen chloride nearly ceases. The product is poured into water and extracted with ether. On removing the ether, the sulphonic chloride remains as an oil, which must be distilled under diminished pressure to avoid decomposition. Many of the sulphonic chlorides are crystalline solids, but their melting-points are usually low. The sulphonic chlorides have the general characters of other acid chlorides, although they do not fume in the air, nor are they very rapidly decomposed by water or dilute alkalis. On the other hand, they combine directly with ammonia and with primary and secondary amines like ethylamine,

or diethylamine, aniline, or methylaniline; but not with tertiary amines—

$$C_6H_5{\cdot}SO_2Cl + 2NH_3 = \underset{\text{Benzene-sulphonamide.}}{C_6H_5{\cdot}SO_2{\cdot}NH_2} + NH_4Cl.$$

$$C_6H_5{\cdot}SO_2Cl + 2NH_2C_6H_5 = \underset{\text{Benzenesulphonanilide.}}{C_6H_5{\cdot}SO_2{\cdot}NHC_6H_5} + C_6H_5NH_2{\cdot}HCl.$$

Both sulphonamides and sulphonanilides are sparingly soluble in water, and are therefore easily separated from the other products of the reaction (in the above example, ammonium chloride and aniline hydrochloride). They are purified by crystallisation from alcohol. Chloramine-*T*, the well-known antiseptic, $CH_3{\cdot}C_6H_4SO_2NClNa$, is prepared by the action of sodium hypochlorite on *p*-toluene sulphonamide.

$$CH_3{\cdot}C_6H_4{\cdot}SO_2NH_2 + NaOCl = CH_3{\cdot}C_6H_4{\cdot}SO_2NClNa + H_2O.$$

The sulphonic chlorides also combine with alcohols and phenols (hydroxybenzenes) in presence of caustic soda solution. Ethyl benzenesulphonate is obtained by warming and shaking a mixture of benzenesulphonic chloride and ethyl alcohol with a solution of caustic soda. It is then extracted with ether, and the ether evaporated—

$$C_6H_5SO_2Cl + C_2H_5OH + NaOH = \underset{\text{Ethyl benzene-sulphonate.}}{C_6H_5{\cdot}SO_2{\cdot}OC_2H_5} + NaCl + H_2O.$$

When benzenesulphonic chloride is heated with phosphorus pentachloride, chlorobenzene is produced. Other sulphonic chlorides behave similarly.

$$C_6H_5SO_2Cl + PCl_5 = C_6H_5Cl + SOCl_2 + POCl_3.$$

We thus see that by the aid of sulphonation, the hydrogen of the benzene nucleus may be replaced by hydroxyl, cyanogen, and chlorine; that insoluble substances may be rendered soluble in water; and that isomeric hydrocarbons in a mixture may be separated from one another.

Questions on Chapter XXXI

1. Describe the preparation of benzenesulphonic acid. How are the sodium, potassium, and calcium salts obtained?

2. In what manner has the process of sulphonation been of advantage technically?

3. What is the result of sulphonation of (1) benzenesulphonic acid, (2) aniline, (3) phenol, and (4) nitrobenzene? State what you consider will be the probable positions taken by the sulphonic group.

4. Describe some of the properties of the sulphonic acids. Explain how benzene, chlorobenzene, phenol, and phenyl cyanide may be obtained from benzenesulphonic acid.

5. Explain and illustrate the use of sulphonation in separating mixtures of hydrocarbons.

6. How is benzenesulphonic chloride obtained? Compare its behaviour as an acid chloride with acetyl chloride.

7. Discuss the structural formula of the sulphonic acids.

CHAPTER XXXII

THE PHENOLS

Phenols.—The name is given to the hydroxy-derivatives of the aromatic hydrocarbons, in which the hydrogen of the nucleus is replaced by hydroxyl. The simplest member of the group is ordinary phenol, or carbolic acid, $C_6H_5(OH)$. It is called a *monohydric* phenol, by which is meant a phenol with one hydroxyl group, and conveys the same idea as monohydric applied to ethyl alcohol (p. 275). If more than one hydrogen atom in benzene is replaced by hydroxyl, the compounds are known as di- and tri-hydric phenols, etc.

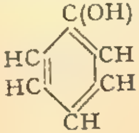
$C_6H_4(OH)_2$.	$C_6H_3(OH)_3$.
Dihydric phenol.	Trihydric phenol.

Structurally, the phenols are analogous to the alcohols, but, as the name carbolic acid implies, they possess a distinctly acid character, inasmuch as they form salts with metallic hydroxides. Ordinary phenol, though sparingly soluble in water, dissolves readily in caustic soda, and on evaporating the solution yields a solid sodium compound. This is sodium phenate or phenoxide, $C_6H_5(ONa)$.

Amyl alcohol, which may be taken for comparison with phenol, is, like phenol, sparingly soluble in water; but the addition of caustic soda produces no change.

It should be remembered that the true analogues of the phenols are the tertiary alcohols containing the group $\vdots C(OH)$; but they exhibit the same indifference to alkalis as the other alcohols.

If we accept Kekulé's formula for benzene, ordinary phenol will have the following structure :—



The acidic character may be connected with the group CH⁚C(OH), also present in acetoacetic ester, which has the property of forming a sodium compound (p. 329).

There is another class of hydroxy-derivatives of the aromatic hydrocarbons which possess the properties of true alcohols. The **aromatic alcohols,** as they are termed, differ in structure from the phenols, inasmuch as they contain the hydroxyl group in the side-chain. Benzyl alcohol, $C_6H_5 \cdot CH_2(OH)$, is a typical aromatic alcohol. The aromatic alcohols will be described in the following chapter (p. 472). Theory demands one monohydroxy-benzene, three dihydroxy-benzenes (ortho, meta, and para), and three tri-hydroxybenzenes. These are all known, as well as the hydroxy-derivatives of toluene, termed **cresols,** and of xylene, called **xylenols,** and many more. They all possess similar properties.

$$\underset{\text{Cresols.}}{CH_3 \cdot C_6H_4(OH).} \qquad \underset{\text{Xylenols.}}{(CH_3)_2 \cdot C_6H_3(OH).}$$

Sources of the Phenols.—Many of the phenols are formed by the destructive distillation of organic matter, *e.g.* wood and coal. Wood-tar and coal-tar are rich in phenols, coal-tar being the main source of ordinary phenol. They are also formed, more especially the di- and tri-hydric phenols, by fusion with caustic potash of resins, tannins (p. 495), and the colouring matters associated with them. Two synthetic methods for the preparation of phenols have been described, one of which, viz. the fusion of the sulphonates with caustic alkalis, has an important technical application (p. 542).

$$C_6H_5SO_3Na + NaOH = C_6H_5(OH) + Na_2SO_3.$$

The second method is the decomposition of diazonium salts with water (p. 433). By the second method all amino-compounds are available for the preparation of phenols. Both reactions offer ready means for obtaining phenols from the hydrocarbons.

Phenol is also made from chlorobenzene by heating it to 350° C. under high pressure with a solution of sodium hydroxide in the presence of copper and cuprous oxide.

Properties of the Phenols.—The phenols are generally colourless, crystalline compounds of low melting-point, many of which may be distilled without decomposition, or are volatile in steam. They

often have a characteristic smell, and possess a strong antiseptic action. The solubility of the phenols in water depends on the proportion of carbon to hydroxyl groups. Ordinary phenol requires 15 parts of water for solution, whereas hydroxy-cymene, $C_{10}H_{13}(OH)$, is nearly insoluble; on the other hand, the di- and tri-hydric phenols are very soluble. They all dissolve in alcohol and ether. With caustic alkalis they form salts or phenates, as already explained; but the phenols being very weak acids, the phenates of the alkalis are strongly alkaline to litmus, and are decomposed even by so feeble an acid as carbonic acid.

EXPT. 160.—Add a few c.c. of water to a few grams of ordinary phenol. Little of the phenol dissolves; but the addition of caustic soda rapidly effects solution. Divide the solution into two parts and add dilute sulphuric acid to one and pass carbon dioxide through the other portion. Provided the solution is sufficiently concentrated, phenol will be precipitated as an oil from both solutions.

The decomposition of the phenates by carbon dioxide is used in the separation of phenols from acids, the sodium salts of which are not affected by carbon dioxide. After saturating the alkaline solution with carbon dioxide, the phenol is separated from the mixture by extraction with ether or distillation in vacuo, whilst the acid remains as the sodium salt in the alkaline solution.

Phenol Ethers and Esters.—When the phenates of the alkalis are boiled with the alkyl halides, phenol ethers, or alkyl phenates, are obtained.

Sodium phenate and methyl iodide yield methyl phenate, phenyl methyl ether, or methoxy-benzene—

$$C_6H_5ONa + CH_3I = \underset{\text{Methyl phenate.}}{C_6H_5OCH_3} + NaI.$$

The methyl ethers are most conveniently prepared by warming the phenol with dimethyl sulphate in alkaline solution—

$$C_6H_5ONa + (CH_3)_2SO_4 = C_6H_5OCH_3 + CH_3NaSO_4.$$

EXPT. 161.—Mix 1 gram of phenol with 1 c.c. of dimethyl sulphate [1] and add 4 c.c. of a 10 per cent. solution of caustic soda. Warm and shake. The odour of phenol is replaced by that of anisole, which can be extracted from the liquid by ether (Ullmann's reaction).

[1] The vapour of dimethyl sulphate is very poisonous and care should be taken not to breathe it.

The phenol-ethers are fragrant smelling liquids or solids, which are insoluble in water. Like the aliphatic ethers they are decomposed by strong hydriodic acid (p. 122). Phenyl methyl ether yields methyl iodide and phenol—

$$C_6H_5OCH_3 + HI = C_6H_5OH + CH_3I.$$

Zeisel's Method.—The reaction just described has been utilised for the identification and estimation of the so-called *methoxyl*, $\cdot OCH_3$, and *ethoxyl*, $\cdot OC_2H_5$, groups in phenol ethers and their derivatives. Compounds of this nature frequently occur among the aromatic constituents of vegetable products and their identification is a matter of importance. The method is known by the name of *Zeisel*, the discoverer, and consists in heating a weighed amount of the substance in a distilling flask with a long neck with strong hydriodic acid in a current of carbon dioxide. The methyl or ethyl iodide which is evolved is passed through an alcoholic solution of silver nitrate, whereby the alkyl iodide is decomposed and silver iodide deposited. The weight of silver iodide represents the weight of alkyl iodide, and consequently determines the presence and number of methoxyl, or ethoxyl, groups in the compound.

Reactions of the Phenols.—Phenols play the part of alcohols not only in giving ethers but in forming esters with acids. When phenol is heated with acetyl chloride or acetic anhydride, the phenyl ester of acetic acid is formed—

$$C_6H_5OH + Cl\cdot COCH_3 = \underset{\text{Phenyl acetate.}}{C_6H_5O\cdot CO\cdot CH_3} + HCl.$$

In the behaviour of the phenols with nitric and sulphuric acids, the benzenoid predominates over the alcoholic character, and in place of nitric and sulphuric esters, such as the alcohols form (p. 189), nitro-derivatives and sulphonic acids are produced; indeed, the presence of hydroxyl greatly facilitates the formation of these compounds. Phenol yields mono-, di-, and tri-nitrophenols with nitric acid, and phenolsulphonic acid with sulphuric acid—

$$C_6H_5OH + HNO_3 = \underset{\text{Nitrophenol.}}{(OH)C_6H_4(NO_2)} + H_2O.$$

$$C_6H_5OH + H_2SO_4 = \underset{\text{Phenolsulphonic acid.}}{(OH)C_6H_4\cdot SO_3H} + H_2O.$$

The amino-phenols are obtained by the reduction of the nitro-compounds, and certain of them have found application in photo-

graphy as developers. *Metol* is *p*-methylaminophenol sulphate, *amidol* is 2:4-diaminophenol hydrochloride. Many of the reactions of the phenols have already been mentioned. The hydroxyl group may be replaced by chlorine or bromine by the action of phosphorus pentachloride or pentabromide (p. 404). The phenols react with diazonium salts to form important azo-dyes (p. 443). Furthermore, by heating phenol with the compounds of zinc chloride, or calcium chloride and ammonia, the hydroxyl is replaced by the amino-group and aromatic amino-compounds result. Phenol yields aniline—

$$C_6H_5OH + NH_3 = C_6H_5NH_2 + H_2O.$$

The reaction has a technical value in connection with the preparation of amino-naphthalene, or naphthylamine (p. 540), which will be referred to again.

When phenols are distilled over hot zinc dust, the hydroxyl is replaced by hydrogen. Ordinary phenol forms benzene—

$$C_6H_5OH + Zn = C_6H_6 + ZnO.$$

The phenols are frequently characterised by colour reactions with ferric chloride. Some phenols (ordinary phenol and resorcinol) give a violet colour, others (the cresols and phloroglucinol) a blue colour, others again (catechol) a green colour. Another colour reaction of the phenols is known as Liebermann's reaction, and has already been described as a test for nitroso-compounds (p. 421). The same reaction may be used as a test for phenols, using sodium or potassium nitrite as the nitroso-compound.

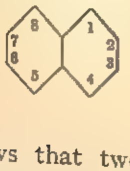
EXPT. 162. *Liebermann's reaction.*—Add a small fragment of solid sodium nitrite to 5 c.c. of strong sulphuric acid, and warm very gently until it is dissolved. Add now about 0·5 gram of phenol. A brown solution is obtained, which, on warming, rapidly changes to deep blue. If the blue solution is poured into water, a cherry-red coloration is produced, which changes to blue again on the addition of caustic soda.

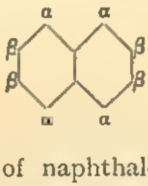
In presence of alkalis, the phenols undergo oxidation, more or less readily, by absorbing oxygen from the air. A solution of a trihydric phenol in alkalis causes immediate absorption of oxygen; and even ordinary phenol, which is comparatively stable in alkaline solution, is converted into di- and tri-hydric phenols on fusion with caustic alkalis (p. 467).

reactions of the aromatic compounds. They are, however, not altogether satisfactory, since they do not account for all the physical properties. For example, the distance between adjacent atoms in a molecule can now be measured accurately, and it has been found that its value is neither that of a single bond nor that of a double bond, but lies between them, and is moreover the same at all parts of the molecule. The modern view is that an entirely new type of structure, called a *resonance* structure (p. 385), is needed to interpret the behaviour not only of aromatic nuclei, but also of a great many other groupings, such, for example, as the carboxyl group. The resonance structure of benzene appears to involve a modification of both double and single bonds of Kekulé's structure to something intermediate in character but completely different from the centric bonds of the Armstrong-Baeyer formula. No satisfactory method has yet been devised of formulating a resonance structure on paper, and its discussion is beyond the scope of this book. For practical purposes we can still use the Kekulé type of formula, or just plain hexagons.

It should be noted that partial reduction of naphthalene to a dihydride leaves in one ring only one double bond which is now definitely olefinic in character, whilst further reduction to tetralin (p. 533) gives a product resembling in its properties an aromatic nucleus with two side-chains in the ortho-position (cp. *o*-xylene). Derivatives of tetralin with substituents in the aromatic nucleus are easily prepared and purified and can be used to prepare corresponding derivatives of naphthalene.

Isomerism of Naphthalene Derivatives.—If we number the positions of the 8 hydrogen atoms arranged round the double hexagon, 1, 2, 3, 4, 5, 6, 7 and 8, we notice that they may be divided into two sets of 4 each, which are symmetrically situated, viz. 1, 4, 5, 8 (these adjoin one of the central carbon atoms) and 2, 3, 6, 7 (these are separated by one carbon atom from one of the central carbon atoms)—





It follows that two mono-derivatives of naphthalene should exist, and in fact two isomers of most of the mono-derivatives of naphthalene are known. The first series is known as α-, the second as β-compounds. The structure of α-naphthol follows from Fittig's

synthesis (p. 534) and the nitro-derivative produced by direct nitration must also be α, as it gives on reduction an amine, which on diazotisation and decomposition leads to the same naphthol. Thus the structure of the β-compounds is deduced by elimination. The number of di-derivatives is easily estimated. Theoretically there are ten, which number also agrees with the experimental results, although the complete set has only been obtained in a few cases. They are indicated by the above numbers, or by the Greek letters α and β. The 1, 2; 1, 3, and 1, 4 positions in the same ring are sometimes referred to as ortho-, meta-, and para-positions; the position 1, 8 is termed the *peri*-position, and resembles an ortho-position; for, if carboxyl groups occupy these two positions, the substance behaves like phthalic acid, and forms an anhydride (p. 497).

In the following pages a brief account is given of the more important naphthalene derivatives, their method of preparation, properties and uses.

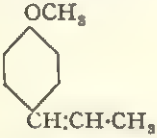
Homologues of Naphthalene.—Some of the alkyl derivatives of naphthalene are found in small quantities in coal-tar. They are also obtained by Fittig's method from bromonaphthalene, the alkyl halide, and metallic sodium (p. 391), or by the Friedel-Crafts reaction from naphthalene and the alkyl halide in presence of aluminium chloride (p. 391).

There are two methyl and two ethyl naphthalenes of which only the β-methyl compound is a solid at the ordinary temperature; it melts at 32°. The other three are liquids with high boiling-points.

Halogen Derivatives of Naphthalene.—These are obtained by precisely the same methods as the corresponding benzene derivatives. α-*Chloronaphthalene* is prepared by passing chlorine through boiling naphthalene, or by heating naphthalene α-sulphonic chloride with phosphorus pentachloride (p. 453). It is a colourless liquid which boils at 263°.

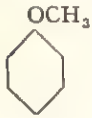
$$\underset{\text{Naphthalene-sulphonic chloride.}}{C_{10}H_7SO_2Cl} + PCl_5 = \underset{\alpha\text{-Chloro-naphthalene.}}{C_{10}H_7Cl} + POCl_3 + SOCl_2.$$

the oxidation of **anethole,** the sweet-smelling constituent of oil of aniseed. The relation of the three compounds is represented by the following formulæ :—



Anethole.

Anisic acid.



Anisole.

Nitrophenols.—Strong nitric acid attacks phenol vigorously and forms resinous products. In order to obtain the mononitro-derivatives, the nitric acid is somewhat diluted with water and the phenol is slowly added. Both ortho- and para-nitrophenol are formed, in accordance with the law of substitution (p. 412). The two substances are separated by distillation in steam. The ortho-compound distils, whereas the para-compound is non-volatile and remains in the distilling flask, from which it is extracted with water. The two isomers present a curious contrast in properties.

The *ortho-compound* has a bright yellow colour, melts at 45° and has a peculiar tarry smell. The *para-compound* is colourless and odourless and melts at 114°. They both form well-crystallised sodium and potassium salts, which are not decomposed by carbon dioxide. The substances are, in fact, stronger acids than phenol, and the property is enhanced with each additional nitro-group (see Picric Acid, below).

p-Nitrophenol is also prepared from *p*-nitracetanilide, which is obtained by nitrating acetanilide in presence of acetic acid. *p*-Nitracetanilide is hydrolysed and converted into *p*-nitraniline, which is then diazotised in the usual way, whereby the amino-group is exchanged for hydroxyl (p. 433). *m*-Nitrophenol is prepared in the same way from *m*-nitraniline (p. 436). *p*-Nitrophenol is used in the preparation of **phenacetin,** or *p*-acetamino-phenetole, $(C_2H_5O)C_6H_4{\cdot}(NH{\cdot}CO{\cdot}CH_3)$, which is used in medicine for neuralgia and headache. The nitrophenol is converted into the nitrophenyl ethyl ether, then reduced to aminophenol, and acetylated—

$$\underset{p\text{-Nitrophenol.}}{(OH)C_6H_4(NO_2)} \rightarrow \underset{p\text{-Nitrophenyl ethyl ether.}}{(C_2H_5O)C_6H_4(NO_2)} \rightarrow \underset{\substack{p\text{-Aminophenetole} \\ \text{(Phenetidine).}}}{(C_2H_5O)C_6H_4(NH_2)}$$

$$\rightarrow \underset{\text{Phenacetin.}}{(C_2H_5O)C_6H_4(NHC_2H_3O).}$$

Other derivatives of *p*-aminophenetole are also used as antipyretics; such are the glycocoll compound, $(C_2H_5O)C_6H_4NH{\cdot}CO{\cdot}CH_2{\cdot}NH_2$, or *phenocoll*, and the lactyl derivative or *lactophenin*. When phenetidine is acted on with carbonyl chloride and subsequently with ammonia, $(C_2H_5O)C_6H_4NH_2 + COCl_2 = (C_2H_5O)C_6H_4NH{\cdot}COCl + HCl$, phenetole carbamide or *dulcin*, $C_2H_5O{\cdot}C_6H_4NH{\cdot}CO{\cdot}NH_2$, is formed, which is an important sweetening agent.

m-Aminophenol and its derivatives are largely used in the manufacture of the important dyes, known as *rhodamines* (p. 526).

Picric Acid, 2-4-6-*Trinitrophenol*, $C_6H_2(OH)(NO_2)_3$, is the final product of the direct nitration of phenol, and is also formed when nitric acid acts on many organic substances, such as silk, wool, leather, etc.

In the manufacture of picric acid phenolsulphonic acid is nitrated in place of phenol, and the formation of tarry and resinous by-products is thereby avoided.

Phenolsulphonic acid is obtained by warming phenol with sulphuric acid on the water-bath (both ortho- and para-sulphonic acids are formed, the ortho-compound predominating when the action occurs at a low temperature, and becoming gradually transformed into the para-compound at 100°). The phenolsulphonic acid is then added slowly to strong nitric acid and subsequently heated.

$$\underset{\text{Phenolsulphonic acid.}}{C_6H_4(OH)SO_3H} + 3HNO_3 = \underset{\text{Picric acid.}}{C_6H_2(OH)(NO_2)_3} + H_2SO_4 + 2H_2O.$$

EXPT. 163. *Preparation of Picric Acid.*—Dissolve about 2 grams of phenol in 2 c.c. of strong sulphuric acid by gently warming; dilute with an equal volume of water; cool, and pour the solution slowly into 6 c.c. of strong nitric acid. Red fumes are evolved. When the action has abated, heat the product on the water-bath for a quarter of an hour with the addition of a little fuming nitric acid, and then pour into cold water. Yellow crystals of picric acid immediately separate.

Picric acid is a lemon-yellow, crystalline compound, melting at 122·5°. It dissolves in water very sparingly with a yellow colour. The petroleum solution, on the other hand, is colourless.[1] The presence of the nitro-groups has the effect of converting phenol

[1] The yellow colour of the aqueous solution is attributed to the dissociation of picric acid into its electro-negative ion, $C_6H_2(NO_2)_3O$,

into a strong acid; for picric acid decomposes carbonates of the metals, and forms a series of well-crystallised salts or *picrates*. Moreover, *picryl chloride*, $C_6H_2(NO_2)_3Cl$, which is obtained by the action of phosphorus chloride on picric acid, is an acid chloride, and forms *picramide*, or trinitraniline, with ammonia. Many of the picrates explode on percussion, although picric acid itself burns quietly when ignited. The fused acid, however, becomes a violent explosive when detonated, and has been used in war under the names of *lyddite* and *melinite*. It also explodes when mixed with lead peroxide and heated.

EXPT. 164.—Mix cautiously a quantity of picric acid, sufficient to be heaped upon a threepenny piece, with rather more than its bulk of red lead; place the mixture in the centre of a metal tray, and heat it with a small flame. The mixture explodes with great violence.

Picric acid has been used for dyeing wool and silk. It has the property of uniting with aromatic hydrocarbons and amino-compounds and forming well-crystallised compounds. The picrate of benzene, $C_6H_6{\cdot}C_6H_2(OH)(NO_2)_3$, is colourless; naphthalene picrate, $C_{10}H_8{\cdot}C_6H_2(OH)(NO_2)_3$, is yellow. Anthracene and many of its homologues form compounds which have a brilliant red colour (p. 547). The compound with aniline has the formula $C_6H_5NH_2{\cdot}C_6H_2(OH)(NO_2)_3$.

The presence of picric acid is sometimes detected by its affinity for wool and silk, which are rapidly dyed a yellow colour in a warm solution without any mordant. When a solution of picric acid is warmed with a solution of potassium cyanide, the liquid becomes a deep violet colour, and deposits, on cooling, a crystalline compound, known as *isopurpuric acid*.

When picric acid is distilled with a paste of bleaching powder and water, a colourless liquid distils, the vapour of which attacks the eyes and mucous membrane and is known as *chloropicrin* (CCl_3NO_2).

When nitrous acid acts upon phenol it forms a compound, which is known as *nitrosophenol* or *quinonoxime*. The compound is an example of tautomerism. It behaves, on the one hand, like a

which is yellow, and hydrogen, the positive ion. In petroleum no dissociation takes place, and the liquid is therefore colourless.

nitroso-compound, giving Liebermann's reaction and aminophenol on reduction. On the other hand, it is prepared like an oxime by the action of hydroxylamine on quinone (p. 482).

Tautomeric forms of Nitrosophenol.

Cresols, *Cresylic acids, Hydroxytoluenes,* $C_6H_4(CH_3)OH$.—The three isomers—*o*-, *m*- and *p*-cresol—are present in coal-tar. The crude cresylic acid is the higher-boiling portion (198°–203°) of the coal-tar phenol which is separated during fractional distillation, or drained from the crystals of phenol. When emulsified with oil or soap, it is used without further treatment as a disinfectant and cheap substitute for phenol. The pure cresols may be obtained by one of the general synthetic methods already described. They give a blue coloration with ferric chloride. Meta-cresol can be nitrated like phenol and forms a trinitro-derivative which is an explosive.

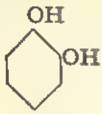
Among the higher monohydric phenols are the hydroxycymenes, **carvacrol** and **thymol,** both of which are vegetable products—

Thymol. Carvacrol.

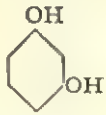
Thymol is a crystalline compound, which is present with cymene in oil of thyme, to which it imparts its fragrant smell. It is used as an antiseptic, and so is its iodine derivative, known as *aristol.* Carvacrol is found in origanum oil (*Origanum hirtum*). It is also obtained from carvone, $C_{10}H_{16}O$, a constituent of caraway oil, by heating with phosphoric acid, and from camphor by distilling with iodine.

THE DIHYDRIC PHENOLS

The dihydroxy-benzenes exist in three isomeric forms; the ortho-compound is called **catechol,** the meta-, **resorcinol,** and the para-, **quinol**—



Catechol.



Resorcinol.

Quinol.

Catechol, $C_6H_4(OH)_2$, was originally obtained by distilling *catechu* (the extract of the Indian *Acacia catechu*),[1] and by fusing certain natural resins with potash. It is also prepared from *o*-phenol-sulphonic acid by fusing the potassium salt with potash—

$$\underset{\text{Potassium-}o\text{-phenol-sulphonate.}}{C_6H_4(OH)SO_3K} + KOH = \underset{\text{Catechol.}}{C_6H_4(OH)_2} + K_2SO_3.$$

A convenient method for obtaining catechol is by the action of hydriodic acid on **guaiacol** or methyl catechol, a colourless liquid which is present in beech-wood tar—

$$\underset{\text{Guaiacol.}}{C_6H_4(OH)OCH_3} + HI = \underset{\text{Catechol.}}{C_6H_4(OH)_2} + CH_3I.$$

The best method, however, is to oxidise *o*-hydroxybenzaldehyde with an alkaline solution of hydrogen peroxide—

$$C_6H_4(OH){\cdot}CHO + H_2O_2 = C_6H_4(OH)_2 + H{\cdot}COOH.$$

Catechol crystallises in colourless plates which melt at 104°. It gives a green coloration with ferric chloride, which changes to red on the addition of sodium bicarbonate solution. This reaction is characteristic of all ortho-dihydric phenols. Catechol reduces Fehling's solution.

Guaiacol carbonate, $[C_6H_4(OCH_3)O]_2CO$, known in commerce as *duotal,* is prepared by the action of carbonyl chloride on guaiacol, and is a useful internal antiseptic.

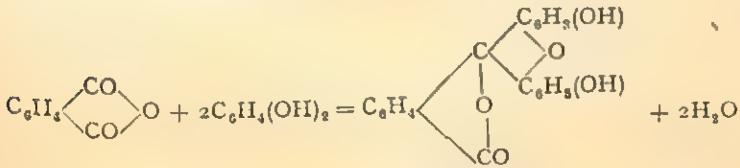
[1] Catechu, or cutch, consists mainly of catechin and a tannin (p. 495), which appear to be chemically related, for they both contain a catechol group in the molecule.

Resorcinol, $C_6H_4(OH)_2$.—Resorcinol can be obtained by a variety of synthetic methods. The industrial process is to fuse the sodium salt of *m*-benzenedisulphonic acid (p. 451) with caustic soda—

$$\underset{\text{Sodium-}m\text{-benzene-disulphonate.}}{C_6H_4(SO_3Na)_2} + 2NaOH = \underset{\text{Resorcinol.}}{C_6H_4(OH)_2} + 2Na_2SO_3.$$

Resorcinol crystallises in colourless needles which melt at 119°. It has a sweetish taste, and is very soluble in water. The reactions of resorcinol resemble those of phenol.

With bromine, tribromoresorcinol is precipitated. Ferric chloride gives a violet coloration. It reduces Fehling's solution and ammonia-silver nitrate like a sugar. Resorcinol is used in the preparation of fluorescein and the eosin dyes (p. 525). The fluorescein reaction is characteristic of meta-dihydric phenols on the one hand, and of anhydrides of dibasic acids, such as succinic acid (p. 350) of the aliphatic series, and phthalic acid (p. 496) of the aromatic series, on the other. Ordinary fluorescein is formed by fusing at 200° a mixture of resorcinol and phthalic anhydride—



Fluorescein.

Fluorescein dissolves in dilute caustic alkalis and in alcohol with a brilliant green fluorescence.

Expt. 165.—Heat together over a small flame about 0·25 gram of phthalic anhydride and 0·5 gram of resorcinol for a minute, taking care not to raise the temperature too high. It is advisable to hold the test-tube a little above the flame. Let the mixture cool, dissolve it in a little caustic soda solution, and pour it into water. The liquid shows a brilliant green fluorescence.

Hexylresorcinol, $C_6H_{11}{\cdot}C_6H_3(OH)_2$, is used as an antiseptic.

Orcinol, *m-Dihydroxytoluene*, $CH_3{\cdot}C_6H_3(OH)_2$, is obtained from *Orcina* and other lichens. Orcinol resembles resorcinol, and gives the fluorescein reaction.

Quinol, *Hydroquinone,* $C_6H_4(OH)_2$.—Quinol is occasionally found among vegetable substances. It is present in bearberry in combination with glucose, as the glucoside, *arbutin.* It is usually obtained from quinone, $C_6H_4O_2$ (p. 481), by reduction with sulphurous acid and extraction with ether—

$$\underset{\text{Quinone.}}{C_6H_4O_2} + H_2O + H_2SO_3 = \underset{\text{Quinol.}}{C_6H_6O_2} + H_2SO_4.$$

EXPT. 166.—Dissolve a few of the yellow crystals of quinone in water, and add sulphurous acid. The solution is decolorised. Extract with a little ether and decant the ethereal solution on to a watch-glass. On evaporation, colourless crystals of quinol are deposited.

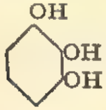
Quinol is readily oxidised to quinone by ferric chloride and other oxidising agents.

EXPT. 167.—Dissolve a few crystals of quinol in water, and add a few drops of ferric chloride. The solution turns yellow and contains quinone. The dirty-green coloration, which is observed on first adding the ferric chloride, is due to the formation of a compound of quinol and quinone, known as *quinhydrone,* $C_6H_4O_2 \cdot C_6H_4(OH)_2$.

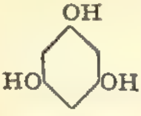
Quinol crystallises in colourless needles which melt at 169°. It is very soluble in water, and its reducing properties in alkaline solution render it a useful photographic developer.

THE TRIHYDRIC PHENOLS

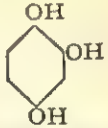
The three trihydroxybenzenes have the following structural formulæ and names :—



Pyrogallol.



Phloroglucinol.



1-2-4-Trihydroxybenzene.

Pyrogallol, *Pyrogallic acid,* $C_6H_3(OH)_3$.—Pyrogallol was first obtained by Scheele in 1786 by heating gallic acid, and the process is still used for its preparation. When gallic acid is heated it loses carbon dioxide—

$$\underset{\text{Gallic acid.}}{C_6H_2(OH)_3COOH} = \underset{\text{Pyrogallol.}}{C_6H_3(OH)_3} + CO_2.$$

Pyrogallol melts at 132° and is very soluble in water. In alkaline solution it rapidly absorbs oxygen and darkens in colour. Among the products of oxidation, acetic acid, carbon dioxide, and a little carbon monoxide have been detected. The property is utilised in gas analysis for estimating oxygen.

EXPT. 168.—Take a long tube closed at one end and furnished with a cork holding a glass tap (Fig. 91). Introduce a few grams of pyrogallol, and then fill the tube with oxygen from a cylinder. Quickly introduce a little solution of caustic soda, close the tube and shake for a minute. On opening the tap under water, water rapidly ascends the tube, indicating absorption of oxygen gas.

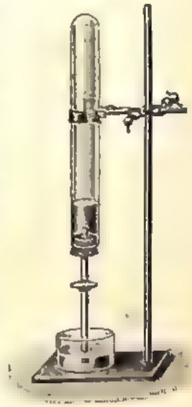


FIG. 91.

Pyrogallol reduces gold, silver, and mercury solutions, and is extensively used as a photographic developer.

It gives a red coloration with ferric chloride, and a blue coloration with ferrous sulphate containing a little ferric chloride.

Phloroglucinol, *symm. Trihydroxybenzene,* $C_6H_3(OH)_3$, is a constituent of certain resins (gamboge, dragon's blood), some of the tannins (p. 495), and certain natural yellow colouring matters, from all of which it is separated by fusion with potash. It is most conveniently prepared from resorcinol by fusion with caustic soda, whereby the resorcinol takes up an additional atom of oxygen from the air—

$$\underset{\text{Resorcinol.}}{C_6H_4(OH)_2} + O = \underset{\text{Phlorglucinol.}}{C_6H_3(OH)_3}.$$

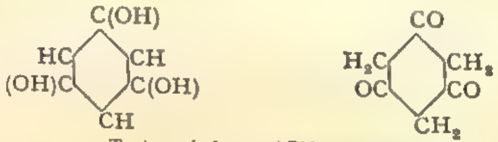
It has also been obtained by synthesis from malonic ester, the details of which cannot be given here, and by condensing malonyl chloride with acetone in presence of water and calcium carbonate—

$$CH_2\left\langle\begin{matrix} COCl \\ \\ COCl \end{matrix}\right. + \left.\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\right\rangle CO = C_6H_3(OH)_3 + 2HCl.$$

Phloroglucinol crystallises with two molecules of water. It gives a blue-violet coloration with ferric chloride, it reduces Fehling's solution, and absorbs oxygen in presence of caustic alkalis. It is

used as a reagent for the pentoses (p. 315). Dissolved in strong hydrochloric acid, it turns pink on warming in presence of a pentose, a reaction which is readily demonstrated with a piece of match-wood containing xylose. Phloroglucinol yields phloroglucitol, $C_6H_9(OH)_3$, on reduction.

Phloroglucinol offers an interesting example of tautomerism (p. 333). On the one hand, it behaves as a trihydric phenol, forming trialkyl and triacyl derivatives. On the other hand, it exhibits the properties of a triketone, and yields a trioxime with hydroxylamine. Moreover, its synthesis from malonyl chloride and acetone (see above) would appear to favour the ketonic structure. The two structural forms will be represented as follows—



Tautomeric forms of Phloroglucinol.

The third isomer, or 1-3-4-**trihydroxybenzene,** has little special interest. It is obtained by fusing quinol with caustic soda, in the same way that resorcinol is converted into phloroglucinol.

Other Hydroxybenzenes.—The potassium salt of hexahydroxybenzene, $C_6(OK)_6$, is formed when carbon monoxide is passed over heated potassium. It is in itself quite stable, but, on standing, undergoes a change and becomes extremely explosive. The compound is a constituent of the black mass which is formed during the distillation of potassium in the course of manufacture. An interesting class of compounds, which have certain points of resemblance with the hexahydric alcohols (p. 275), and hexoses (p. 288), are the hydroxy-derivatives of hexahydrobenzene, C_6H_{12}. *Quercitol*, $C_6H_7(OH)_5$, is found in acorns. It is a crystalline substance with a sweet taste, and dissolves in water, but does not ferment. *Inositol*, $C_6H_6(OH)_6$, of which two active forms and one inactive form are known, is contained in unripe peas and beans. These substances appear to take the place of the vegetable carbohydrates.

Questions on Chapter XXXII

1. Explain the meaning of the term *phenol*.—Compare and contrast amyl alcohol and ordinary phenol. Is this comparison with amyl alcohol a legitimate one?

2. Give examples of mono-, di-, and tri-hydric phenols. Name any properties by which a phenol may be distinguished from a member of any of the previous groups of compounds, and devise a method for separating ordinary phenol from (1) benzene, (2) chlorobenzene, (3) nitrobenzene, and (4) aniline.

3. Give a list of the natural sources of the phenols, and describe the preparation of carbolic acid from coal-tar.

4. In what manner may the phenols be obtained from the hydrocarbons? Mention two methods.

5. Describe a method for separating the phenols from organic acids. Illustrate this in the case of a mixture of acetic acid and carbolic acid.

6. Describe and explain Zeisel's method for estimating *methoxyl* and *ethoxyl* groups in phenol ethers. Calculate the number of methoxyl groups in a compound of the formula $C_8H_8O_3$ from the following data: 0·2338 gram of substance gave 0·3598 gram of silver iodide.

7. How can phenol be (1) obtained from benzene and aniline; and (2) converted into benzene and aniline? Describe the action of the following reagents on phenol: (1) caustic soda, (2) bromine, (3) phosphorus pentabromide, (4) nitric acid, (5) sulphuric acid, and (6) acetyl chloride.

8. Describe Liebermann's test for phenols. What other reactions are characteristic of the phenols as a class?

9. Describe methods of preparing and distinguishing the three isomeric dihydroxybenzenes.

10. Mention some of the properties of pyrogallol. How is it distinguished from phloroglucinol?

11. How are the three mononitrophenols obtained? How are the ortho- and para-compounds distinguished, and for what purpose is the para-compound employed?

12. Describe the preparation of picric acid. Why is it termed an acid? Compare it with carbolic acid. What are its technical uses?

13. What is *anisole?* In what relation does it stand to aniseed oil? How can anisole be synthesised?

CHAPTER XXXIII

AROMATIC ALCOHOLS, ALDEHYDES, KETONES, AND QUINONES

Aromatic Alcohols

If hydrogen in the side-chain of an aromatic hydrocarbon is replaced by hydroxyl, the aromatic alcohols result. Little more need be said about these compounds than that they resemble the aliphatic alcohols, both in their method of preparation and in their chemical properties (p. 98). They are naturally less soluble in water than the simpler members of the aliphatic series by reason of the large proportion of carbon to hydroxyl; their higher boiling-points are due to their higher molecular weights; but they form esters with acids and undergo oxidation to aldehydes, ketones, and acids, after the usual manner of alcohols. The most important features of the aromatic alcohols may be best illustrated by studying benzyl alcohol, the simplest member of the group.

Benzyl Alcohol, $C_6H_5{\cdot}CH_2(OH)$, is isomeric with the cresols It is found in Peru and Tolu balsam and in storax (the exudation from *Styrax officinalis*, a shrub which grows in the East) as the benzyl ester of benzoic and cinnamic acids (p. 501).

Benzyl alcohol is most easily prepared by boiling benzyl chloride with a solution of potassium carbonate until the pungent smell of the chloride vanishes.

$$2C_6H_5{\cdot}CH_2Cl + K_2CO_3 + H_2O = \underset{\text{Benzyl alcohol.}}{2C_6H_5{\cdot}CH_2(OH)} + 2KCl. + CO_2.$$

The product is extracted with ether, which dissolves the alcohol; the ether is removed and the benzyl alcohol distilled.

Benzyl alcohol is also obtained by the action of caustic potash solution on benzaldehyde. Two molecules of benzaldehyde take

part in the reaction, one molecule being oxidised to benzoic acid at the expense of the other, which is reduced to benzyl alcohol—

$$\begin{array}{l} C_6H_5C\boxed{H\,O + C_6H_5CHO} \\ \quad + \quad OK \qquad\qquad\quad H \end{array} = \underset{\text{Potassium benzoate.}}{C_6H_5COOK} + \underset{\text{Benzyl alcohol.}}{C_6H_5{\cdot}CH_2(OH)}.$$

The semi-solid product is dissolved in water and extracted with ether, which separates the benzyl alcohol from the potassium benzoate.

This reaction is specially characteristic of aromatic aldehydes which contain the aldehyde group in the nucleus, and is known as Cannizzarro's reaction. Formaldehyde (p. 133) and glyoxal (p. 321) behave similarly, but most of the aliphatic aldehydes resinify. Benzyl alcohol can also be prepared by the hydrolysis of its esters.

It is a colourless liquid with a faint aromatic smell which boils at 206° and is moderately soluble in water. It possesses anæsthetic properties. It is readily distinguished from the isomeric cresols by its smell, and by its behaviour with caustic soda, hydrochloric and nitric acids. Benzyl alcohol, unlike the cresols, does not dissolve in caustic soda more readily than it does in water; on warming benzyl alcohol with strong hydrochloric acid, the liquid, which is at first clear, becomes turbid from the separation of fine drops of benzyl chloride which gradually rise and form a layer on the surface.

$$C_6H_5CH_2OH + HCl = C_6H_5CH_2Cl + H_2O.$$

When strong nitric acid is added slowly to benzyl alcohol, heat is developed and nitrous fumes are evolved. When the action has ceased and a little alkali is added to neutralise the acid, the smell of benzaldehyde is at once perceived.

$$2C_6H_5CH_2OH + 2HNO_3 = 2C_6H_5CHO + 3H_2O + N_2O_3.$$

AROMATIC ALDEHYDES

The aldehydes, like the hydroxy-compounds, may be divided into two classes, those which contain the aldehyde group in the side-chain and those in which it is present in the nucleus. There is not, however, that marked difference in the properties of the two classes of compounds which separates the aromatic alcohols

from the phenols. There are certain minor differences to which attention will be drawn; but, broadly speaking, they resemble one another as well as the aliphatic aldehydes. Like the aliphatic compounds, the aromatic aldehydes undergo an unusual variety of chemical changes, many of which must be omitted for want of space. As in the foregoing chapters, we shall study the group by selecting from it a common and typical member.

Benzaldehyde, *Oil of Bitter Almonds*, $C_6H_5{\cdot}CHO$.—Few compounds have played so important a *rôle* in the development of organic chemistry as benzaldehyde; whether we consider it historically, as affording by its chemical changes the first clear conception of the term compound radical (p. 83), or chemically, as marking the rapid progress of synthetic organic chemistry.

Benzaldehyde was originally obtained from bitter almonds, in which, as Wöhler showed, it is present as the glucoside, *amygdalin* (p. 212). When amygdalin is boiled with dilute acids, it is hydrolysed and yields benzaldehyde, hydrocyanic acid, and glucose. The same change occurs if the almonds are crushed in a mortar with a few drops of water. In the second case, the ferment *emulsin* which is present in the almonds is the hydrolytic agent. The benzaldehyde may be removed by distilling in steam, and purified by the method described below.

Expt. 169.—Grind up a few bitter almonds with a little water in a mortar, and leave them for half an hour. The smell of the aldehyde and of hydrocyanic acid will be perceived.

Benzaldehyde is prepared by the oxidation of benzyl alcohol with strong nitric acid or nitrogen tetroxide (p. 473), or by distilling a mixture of calcium benzoate and calcium formate (p. 129).

$$\begin{array}{l} C_6H_5COOca' \\ + HCOOca' \end{array} = \underset{\text{Benzaldehyde.}}{C_6H_5CHO} + CaCO_3.$$

Another method is to oxidise toluene, diluted with carbon bisulphide, by means of chromium oxychloride. A brown precipitate is formed, which is separated by filtration and decomposed with water. The composition of the precipitate is not known, but, on adding water, it yields benzaldehyde and chromic chloride. It can also be obtained by the reduction of benzoyl chloride with

hydrogen in presence of palladium. The laboratory method of preparing benzaldehyde is to oxidise benzyl chloride by boiling it with a solution of copper nitrate—

$$2C_6H_5\cdot CH_2Cl + Cu(NO_3)_2 = 2C_6H_5CHO + CuCl_2 + 2HNO_2.$$

The product is distilled in steam, and the distillate, which contains the aldehyde, is extracted with ether.

It is manufactured on a large scale from benzal chloride by heating it with milk of lime under pressure in an iron vessel—

$$C_6H_5CHCl_2 + Ca(OH)_2 = C_6H_5CHO + CaCl_2 + H_2O.$$

Benzaldehyde can be readily purified by converting it into the crystalline bisulphite compound, which is washed with ether to remove impurities, and then decomposed with dilute sulphuric acid in a current of steam—

$$C_6H_5CH(OH)SO_3Na + H_2SO_4 = C_6H_5CHO + NaHSO_4 + H_2O + SO_2$$

Expt. 170.—Shake up a few c.c. of benzaldehyde with an equal volume of a strong solution of sodium bisulphite. It immediately solidifies to a mass of crystals of the bisulphite compound.

Properties of Benzaldehyde.—Benzaldehyde is a colourless liquid which boils at 179° and possesses a fragrant smell of bitter almonds. It quickly oxidises on exposure to the air and forms benzoic acid. A bottle of benzaldehyde will generally contain crystals of benzoic acid in the neck.

The process is not one of ordinary oxidation; for it is a remarkable fact that strong nitric acid does not oxidise benzaldehyde in the cold, but forms the nitro-derivative (p. 477). It appears that during oxidation in air benzaldehyde first takes up a molecule of oxygen and forms the peroxide of benzoic acid, $C_6H_5\cdot CO_2\cdot OH$, which acts as the oxidising agent in the process, yielding oxygen to another benzaldehyde molecule and becoming itself converted into benzoic acid.

Benzaldehyde gives Schiff's reaction (p. 134). It slowly reduces ammonia-silver nitrate and alkaline copper solution, which may be in part accounted for by its insolubility in water. It forms a bisulphite compound described in Expt. 170, and a cyanhydrin with hydrocyanic acid—

$$C_6H_5CHO + HCN = \underset{\text{Benzaldehyde cyanhydrin.}}{C_6H_5CH(OH)CN.}$$

With phenylhydrazine, benzaldehyde forms a phenylhydrazone, $C_6H_5CH{:}N{\cdot}NHC_6H_5$.

Expt. 171.—Make a dilute solution of phenylhydrazine acetate (p. 132), and add it to a drop of benzaldehyde. A yellow, crystalline precipitate of the hydrazone is thrown down.

With hydroxylamine, benzaldehyde yields benzaldoxime, $C_6H_5CH{:}N{\cdot}OH$.

$$C_6H_5CH\boxed{O + H_2}NOH = \underset{\text{Benzaldoxime.}}{C_6H_5{\cdot}CH{:}NOH} + H_2O.$$

In reality, two oximes of benzaldehyde are known; one is obtained by adding hydroxylamine hydrochloride to the benzaldehyde mixed with caustic soda and extracting the benzaldoxime with ether. The second is prepared by passing hydrochloric acid into the ethereal solution of the first aldoxime; the hydrochloride of the second benzaldoxime is formed, from which the oxime is liberated by the addition of alkali and extraction with ether. The first melts at 34°; the second melts at 130°, becoming slowly transformed into the lower-melting compound. The difference between the two compounds is attributed to a space arrangement of the atoms, of the same character as that described under fumaric and maleic acids (p. 366). The two stereoisomers are usually represented by the following formulæ, and are distinguished by the names *syn* and *anti*, which correspond to *cis* and *trans* among the stereo-isomeric acids.

$$\begin{array}{c} C_6H_5{\cdot}CH \\ \| \\ \quad N{\cdot}OH. \end{array} \qquad\qquad \begin{array}{c} C_6H_5{\cdot}CH \\ \| \\ HO{\cdot}N \quad \end{array}$$

β or Benz*syn*aldoxime, m.p. 130°. α or Benz*anti*aldoxime, m.p. 34°.

This theory of the isomerism of the benzaldoximes is due to Hantzsch and Werner. Similar relations exist among the isomeric oximes of the aromatic ketones (p. 479).

So far benzaldehyde exhibits a close correspondence with the aliphatic aldehydes. It is distinguished from them by its behaviour with the caustic alkalis, ammonia, and potassium cyanide. The action of caustic potash on benzaldehyde in producing benzyl alcohol and benzoic acid has already been described (p. 473). When strong ammonia solution is added to benzaldehyde, a crystalline compound is gradually deposited, which is not an aldehyde-ammonia, but a substance known as **hydrobenzamide**, and is formed as follows—

$$3C_6H_5CHO + 2NH_3 = \underset{\text{Hydrobenzamide.}}{(C_6H_5CH)_3N_2} + 3H_2O.$$

At a low temperature an aldehyde-ammonia of the formula $(C_6H_5CHO)_2NH_3$ is formed.

When benzaldehyde is boiled with an aqueous-alcoholic solution of potassium cyanide, condensation of two molecules of the aldehyde occurs, resembling the aldol condensation (p. 134). The product is called **benzoin,** and is a colourless, crystalline compound melting at 137°

$$2C_6H_5CHO = \underset{\text{Benzoin.}}{C_6H_5{\cdot}CHOH{\cdot}CO{\cdot}C_6H_5}$$

Benzoin is an alcoholic ketone, which is easily oxidised by nitric acid to the diketone, **benzil,** $C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5$. When boiled with alcoholic potash benzil undergoes rearrangement to a salt of *benzilic acid,*

$$C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5 + KOH = \underset{\text{Potassium benzilate.}}{(C_6H_5)_2{\cdot}C{<}\begin{matrix}OH\\COOK\end{matrix}}$$

Benzaldehyde is used in the manufacture of *benzaldehyde (malachite) green* and other colours; in the preparation of *cinnamic acid,* and for a variety of synthetic processes, some of which will be referred to in later chapters.

When benzaldehyde is added to strong nitric acid it dissolves, and, following the rule laid down on p. 412, forms mainly the meta-compound. The ortho-compound is obtained by oxidising *o*-nitrobenzyl alcohol with nitrogen tetroxide. *o*-Nitrobenzaldehyde has a special interest from the ease with which it is converted into indigo (p. 529). The para-compound is formed by the oxidation of *p*-nitrotoluene.

Among the other aromatic aldehydes, **cuminol,** or *p*-isopropylbenzaldehyde, and **cinnamic aldehyde,** or phenyl acrolein, are of interest. Cuminol is present in *cumin oil;* cinnamic aldehyde is the chief constituent of *cinnamon* and *cassia oil.* Cinnamic aldehyde is also obtained by the action of a solution of caustic soda on a mixture of benzaldehyde and acetaldehyde. This reaction, which takes place between aromatic aldehydes and many aldehydes and ketones containing the group $CH_2{\cdot}CO$, is known as **Claisen's reaction,** and recalls the formation of crotonaldehyde from acetaldehyde (p. 271).

$$C_6H_5{\cdot}CHO + CH_3{\cdot}CHO = \underset{\text{Cinnamic aldehyde.}}{C_6H_5{\cdot}CH{:}CH{\cdot}CHO} + H_2O.$$

On oxidation, cinnamic aldehyde is first converted into cinnamic

acid (p. 501), the side-chain then breaks down and benzoic acid is formed.

Aromatic Ketones.

The aliphatic ketones contain two alkyl radicals linked by a ketone group. In the aromatic ketones, one radical is aromatic, the other may be aliphatic or aromatic. **Acetophenone**, or phenylmethyl ketone, and **benzophenone**, or diphenyl ketone, are two typical examples of aromatic ketones—

$C_6H_5 \cdot CO \cdot CH_3$. Acetophenone, or Phenylmethyl ketone.	$C_6H_5 \cdot CO \cdot C_6H_5$. Benzophenone, or Diphenyl ketone.

The aromatic ketones are usually crystalline substances with a pleasant smell, which in chemical characters resemble the aliphatic ketones. The methods of preparation will be illustrated in the case of acetophenone and benzophenone.

Acetophenone, *Phenylmethyl ketone,* $C_6H_5 \cdot CO \cdot CH_3$, is obtained by distilling a mixture of calcium benzoate and acetate—

$$\begin{matrix} C_6H_5 | COOca' \\ CH_3 \cdot CO | Oca' \end{matrix} = \underset{\text{Acetophenone.}}{C_6H_5 \cdot CO \cdot CH_3} + CaCO_3.$$

A more convenient method is that of Friedel and Crafts already referred to (p. 391), in which a mixture of benzene, acetyl chloride, and aluminium chloride are allowed to react—

$$C_6H_6 + ClCO \cdot CH_3 \, [+ AlCl_3] = C_6H_5 \cdot CO \cdot CH_3 + HCl.$$

When the reaction, which proceeds spontaneously, is complete, the product is shaken with caustic soda solution, and the undissolved oil removed and distilled.

Acetophenone is a colourless, crystalline compound with a fragrant smell which melts at 20° and boils at 202°. It is sometimes used as a hypnotic, under the name of *hypnone.* On reduction it yields the secondary alcohol, phenylmethyl carbinol, $C_6H_5 \cdot CH(OH) \cdot CH_3$, and on oxidation, benzoic acid, the aliphatic side-chain being removed. Acetophenone forms an oxime and a phenylhydrazone, and possesses the general characters of an aliphatic ketone.

Benzophenone, *Diphenyl ketone,* $C_6H_5 \cdot CO \cdot C_6H_5$, is obtained by distilling calcium benzoate, and by the action of benzoyl chloride,

or carbonyl chloride, on benzene in presence of aluminium chloride.

$$C_6H_6 + ClCO{\cdot}C_6H_5 \,[+ AlCl_3] = C_6H_5{\cdot}CO{\cdot}C_6H_5 + HCl.$$
$$2C_6H_6 + COCl_2 \,[+ AlCl_3] = C_6H_5{\cdot}CO{\cdot}C_6H_5 + 2HCl.$$

It is a fragrant smelling, crystalline substance, which melts at 48° and boils at 162°. On reduction with sodium amalgam it gives the secondary alcohol, *benzhydrol*, $C_6H_5{\cdot}CH(OH){\cdot}C_6H_5$, and also *benzpinacol*, $(C_6H_5)_2C(OH){\cdot}C(OH)(C_6H_5)_2$ (p. 130). By using a stronger reducing agent, such as hydriodic acid, benzophenone is converted into diphenylmethane, $C_6H_5{\cdot}CH_2{\cdot}C_6H_5$.

Examples of stereo-isomeric ketoximes similar to those of the benzaldoximes (p. 476) are not uncommon, where the two radicals attached to the ketone group are different. Chlorobenzophenone, when converted into the oxime, yields two products of different melting-points, which are represented by the following space formulæ—

$$\begin{array}{c} ClC_6H_4{\cdot}C{\cdot}C_6H_5 \\ \| \\ HO{\cdot}N. \end{array} \qquad\qquad \begin{array}{c} ClC_6H_4{\cdot}C{\cdot}C_6H_5 \\ \| \\ N{\cdot}OH. \end{array}$$

Phenolic Alcohols and Aldehydes

A number of substances are known which possess the double function of phenol and alcohol as well as of phenol and aldehyde. In one group the properties are determined by the presence of hydroxyl groups, both in the side-chain and nucleus; in the other by the presence of an aldehyde group together with a nuclear hydroxyl. Many of these compounds possess an agreeable aroma, and derive an interest from their occurrence among plant products. It is to these especially that attention will be directed.

Saligenin, *o-Hydroxybenzyl alcohol*, $C_6H_4(OH)CH_2OH$, is found combined with glucose in the glucoside, **salicin**, which occurs in the bark of the willow (*Salix*) and in poplar buds. It is prepared synthetically by the reduction of salicylic aldehyde (see below). It is a crystalline substance, which melts at 82°, and gives a deep blue colour with ferric chloride.

Salicylaldehyde, *o-Hydroxybenzaldehyde*, $C_6H_4(OH)CHO$, is found in the volatile oil of certain kinds of spiræa, and is also obtained by the oxidation of saligenin. An interesting synthetic

method is that known as **Reimer's reaction,** by which both the *o*- and *p*-hydroxybenzaldehydes are formed. It consists in heating together a mixture of phenol, chloroform, and sodium ethoxide or caustic potash—

$$C_6H_5OH + CHCl_3 + 4KOH = KO{\cdot}C_6H_4{\cdot}CHO + 3KCl + 3H_2O.$$

The product is acidified, to liberate the hydroxyaldehydes from the potassium salts, and distilled in steam. The ortho-compound, which is a volatile oil, distils; the para-compound, which is a solid, remains in the distilling flask, and is extracted with water.

Another interesting method for preparing aldehydes of the phenol ethers is to act on the phenol ether with the hydrochloride of hydrocyanic acid, $HCN{\cdot}HCl$, in presence of aluminium chloride. The imide is first formed, which decomposes on warming into the aldehyde and ammonia. Anisole gives anisaldehyde, or *p*-methoxybenzaldehyde. The two stages in the reaction are represented as follows—

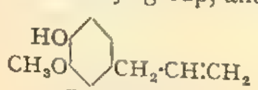
1. $C_6H_5OCH_3 + HCN{\cdot}HCl = C_6H_4(OCH_3)CH{:}NH + HCl.$
2. $C_6H_4(OCH_3)CH{:}NH + H_2O = C_6H_4(OCH_3)CHO + NH_3.$
   Anisaldehyde.

Anisaldehyde, $CH_3O{\cdot}C_6H_4{\cdot}CH{:}O$, is obtained from oil of aniseed, the chief constituent of which is *anethole* (p. 462), which can be oxidised to anisaldehyde and anisic acid. It has been synthesised by the action of methyliodide on *p*-hydroxybenzaldehyde and alcoholic potash.

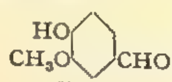
Vanillin, *m-Methoxy*-p-*hydroxybenzaldehyde,*

$$C_6H_3(OH)(OCH_3){\cdot}CHO,$$

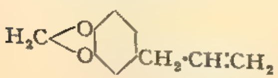
is the sweet-smelling constituent of the vanilla-pods, and sublimes from the pods on heating, in fine, colourless needles which melt at 80°. It is prepared from **eugenol,** the chief constituent of oil of cloves. Vanillin has also been obtained from guaiacol (p. 466) by means of Reimer's reaction. When oxidised, the aldehyde group becomes a carboxyl group, and *vanillic acid* is formed.



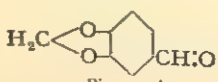
Eugenol.



Vanillin.



Safrole.



Piperonal.

Piperonal, *heliotropin* $C_8H_6O_3$, the methylene ether of protocatechuic aldehyde, is prepared from safrole (p. 494) and on oxidation gives piperonylic acid.

Quinones

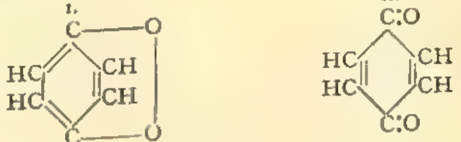
The quinones form a peculiar class of substances which have no representatives among the aliphatic compounds. They are obtained by the oxidation of para-hydroxy- and amino-derivatives of benzene and its homologues.

Benzoquinone, *Quinone,* $C_6H_4O_2$, was originally obtained by the oxidation of quinic acid (p. 496), which is found in cinchona bark associated with the cinchona alkaloids (p. 585), but has chemically no connection with the alkaloid, quinine. It is formed when quinol, *p*-aminophenol, or *p*-phenylenediamine is oxidised; but it is usually prepared by the oxidation of aniline in the cold, with potassium dichromate and sulphuric acid. The dark product is extracted with ether, which dissolves the quinone, and on removing the ether, benzoquinone crystallises in golden-yellow prisms, which melt at 116° and sublime without decomposition, emitting a peculiar smell and acrid vapours. The course of this somewhat complex chemical change will be better understood when the structure of quinone has been discussed.

Structure of Quinone.—The constitution of quinone is derived from a study of its various reactions, and especially from its close relationship to quinol (p. 468).

It was stated on p. 468 that quinol gives quinone on oxidation. The process may occur in two ways, represented by the following formulæ—

I. II.



Quinone.

Formula I. represents a peroxide, examples of which are known among the derivatives of the acids, *e.g.* benzoyl and acetyl peroxide, which have the general formula—

$$\begin{array}{l} R'\cdot CO\cdot O \\ \qquad\quad\ | \\ R'\cdot CO\cdot O. \end{array}$$

These substances agree with quinone in so far as they are all oxidising agents; but, on the other hand, the fact that quinone combines with hydroxylamine and forms both a mono- and a di-oxime, is strongly in favour of the diketone formula represented in Formula II.

$O:C_6H_4:NOH$ — Quinone monoxime.

$HON:C_6H_4:NOH$ — Quinone dioxime.

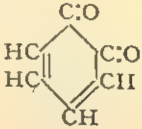
Moreover, the existence of the pair of double bonds, which the second formulæ necessitates, is supported by the fact that quinone forms a di- and tetra-chloride with chlorine, $C_6H_4O_2Cl_2$, $C_6H_4O_2Cl_4$, and similar compounds with bromine.

A number of intermediate products are formed during the oxidation of aniline, among them being the dyestuff *aniline black*, but the final product is quinone.

When quinone is reduced to quinol an intermediate product, known as *quinhydrone*, $C_6H_4O_2{\cdot}C_6H_4(OH)_2$, is obtained in the form of lustrous green crystals (p. 468).

Chloranil, *Tetrachloroquinone*, $C_6Cl_4O_2$, has already been referred to (p. 461) as a product obtained by oxidising phenol with potassium chlorate and hydrochloric acid. It is also obtained in a similar way from aniline, *p*-phenylenediamine, and other substances. Chloranil is occasionally employed as an oxidising agent for organic substances.

Ortho-quinone, prepared by oxidising catechol dissolved in ether with dry silver oxide, is a red crystalline substance without smell and non-volatile (see p. 544).



Ortho-quinone.

Questions on Chapter XXXIII

1. Describe two methods of obtaining benzyl alcohol. How would you distinguish benzyl alcohol from the isomeric phenols? Give the formulæ of the latter compounds.

2. Describe two methods by which benzaldehyde is prepared. Give details of the process, including the method of purification.

3. How would you prove by its properties and reactions that the chief constituent of bitter almond oil is an aldehyde? In what respect do such aldehydes differ from acetic aldehyde?

4. Explain the theory which accounts for the existence of two benzaldoximes.

5. Describe the action of the following reagents on benzaldehyde: (1) potassium cyanide, (2) caustic potash, (3) ammonia, (4) nitric acid. Explain the conditions of each reaction, and the method you propose for isolating the products.

6. What is Claisen's reaction? Describe the artificial preparation of cinnamic aldehyde. What products does cinnamic aldehyde yield on oxidation?

7. Describe a method for preparing aromatic ketones, and give an example of their behaviour with reducing agents.

8. What is meant by "Reimer's reaction"? Describe the preparation of (1) salicylaldehyde from phenol, and (2) vanillin from guaiacol by this reaction.

9. How is quinone prepared? What evidence is there that this compound does not contain hydroxyl, and how is it converted into a substance which does?

CHAPTER XXXIV

THE AROMATIC ACIDS

The Aromatic Acids derive their properties as acids from the presence of the carboxyl group, which may be either in the nucleus or side-chain of the aromatic compound. The isomers, toluic and phenylacetic acid are examples of the two classes of compounds—

$$\underset{\text{Toluic acid.}}{CH_3C_6H_4{\cdot}COOH.} \qquad \underset{\text{Phenylacetic acid.}}{C_6H_5{\cdot}CH_2{\cdot}COOH.}$$

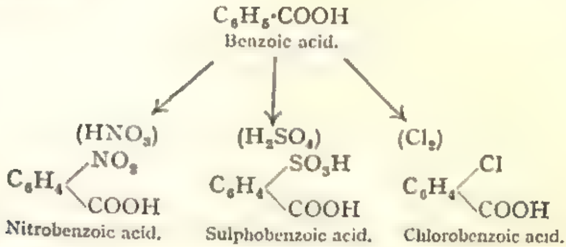
The general properties of both classes resemble those of the aliphatic acids. They form salts with metals, esters with the alcohols, acid chlorides, anhydrides, and amides by similar methods. The following derivatives of benzoic acid may be taken for illustration, by the side of which the corresponding derivatives of acetic acid are placed for comparison :—

$C_6H_5{\cdot}CO{\cdot}ONa$	Sodium benzoate.	$CH_3{\cdot}CO{\cdot}ONa$	Sodium acetate.
$C_6H_5{\cdot}CO{\cdot}OC_2H_5$	Ethyl benzoate.	$CH_3{\cdot}CO{\cdot}OC_2H_5$	Ethyl acetate.
$C_6H_5{\cdot}CO{\cdot}Cl$	Benzoyl chloride.	$CH_3{\cdot}CO{\cdot}Cl$	Acetyl chloride.
$\begin{matrix} C_6H_5{\cdot}CO \\ \quad\rangle O \\ C_6H_5{\cdot}CO \end{matrix}$	Benzoic anhydride.	$\begin{matrix} CH_3{\cdot}CO \\ \quad\rangle O \\ CH_3{\cdot}CO \end{matrix}$	Acetic anhydride.
$C_6H_5{\cdot}CO{\cdot}NH_2$	Benzamide.	$CH_3{\cdot}CO{\cdot}NH_2$	Acetamide.

Any difference in properties between the aromatic and aliphatic acids may generally be ascribed (1) to the larger proportion of carbon to carboxyl in the aromatic acids, which decreases the solubility in water; (2) to the higher molecular weight, which renders the substance less volatile (the aromatic acids are crystalline solids); (3) to the presence of the benzene nucleus, which increases the strength of the acid, as determined from its augmented dissociation constant (p. 146).

The aromatic acids, like the hydrocarbons, are acted upon by

chlorine, bromine, and nitric and sulphuric acids, and give substitution products from which amino-acids, hydroxy-acids, and other derivatives may be obtained by means of the reactions already studied.



By replacing more than one hydrogen atom by carboxyl, either in the nucleus or side-chain, polybasic acids are obtained. Examples of dibasic acids are the three phthalic acids (p. 496). The carboxyl is readily replaced by hydrogen by distilling the acid, or its calcium salt with lime, or, in some cases, by the action of heat alone. An example of the first is benzoic acid, which gives benzene on distillation with lime (p. 388); of the second, gallic acid, which loses carbon dioxide on simply heating, forming pyrogallol (p. 468).

Many of the acids are found in Nature as constituents of plants and, occasionally, of animal products. As a rule, they are more readily prepared by one or other of the numerous synthetic methods, which are described under benzoic acid.

Benzoic Acid, $C_6H_5 \cdot COOH$, has long been known, and was originally obtained by heating gum-benzoin, a resin obtained by incisions made into the stem of *Styrax benzoin,* a tree which is indigenous to Sumatra and Java. The true composition of benzoic acid was determined by Liebig and Wöhler in 1832. They discovered some of the derivatives enumerated above (p. 484) and many others, and showed that the same group of elements, C_7H_5O (now written, $C_6H_5 \cdot CO$), which they termed *benzoyl,* ran through the whole series of compounds. These were the facts which they embodied in their classical research on "The Radical of Benzoic Acid" (p. 3), wherein they placed the theory of the compound radical for the first time on a secure foundation.

EXPT. 172.—The formation of benzoic acid from gum-benzoin is readily shown as follows: Place a little of the resin in a porcelain

basin, cover it with a cone made out of filter paper, and heat it gently on a sand-bath over a small flame. The resin fuses, and crystals of benzoic acid sublime into the paper cone, emitting at the same time a smell resembling incense.

Benzoic acid is present in the resin chiefly in the form of the ester of benzyl alcohol. A small amount of the same ester is also found in Peru and Tolu balsam. Another source of benzoic acid is **hippuric acid,** which is present in the urine of horses and cattle and other herbivorous animals, and has already been referred to under glycine (p. 325).

Preparation of Benzoic Acid.—Benzoic acid is obtained by the following general synthetic methods, which may be applied to the preparation of other acids of the series :—

1. By hydrolysis of phenyl cyanide, or benzonitrile, usually by boiling with moderately strong sulphuric acid (p. 489).

$$\underset{\text{Benzonitrile.}}{C_6H_5CN} + 2H_2O = \underset{\text{Benzoic acid.}}{C_6H_5{\cdot}COOH} + NH_3.$$

As the cyanides are easily obtained from the amino-compounds by means of the diazo-reaction, as well as from the sulphonic acids, the method is available for preparing both the acid and its derivatives.

2. By the oxidation of aromatic compounds containing one side-chain, and even more readily, if the side-chain is substituted. Toluene can be oxidised to benzoic acid by heating it with dilute nitric acid in a sealed tube; but if benzyl chloride, benzyl alcohol, benzaldehyde, or acetophenone is taken, the reaction is facilitated, and boiling with potassium permanganate is sufficient to effect oxidation.

Derivatives of toluene, which are substituted in the nucleus, undergo a similar change, and yield the corresponding derivatives of benzoic acid (p. 396). Chlorotoluene gives chlorobenzoic acid—

$$Cl{\cdot}C_6H_4{\cdot}CH_3 + 3O = \underset{\text{Chlorobenzoic acid.}}{Cl{\cdot}C_6H_4{\cdot}COOH} + H_2O.$$

3. The Friedel-Crafts reaction is the basis of two methods for preparing aromatic acids. When benzene and carbonyl chloride react in presence of aluminium chloride, benzoyl chloride is formed, which yields the acid when decomposed by water (p. 488)—

$$C_6H_6 + COCl_2[+ AlCl_3] = \underset{\text{Benzoyl chloride.}}{C_6H_5{\cdot}COCl} + HCl.$$

The materials are the same as those used in preparing benzophenone, but the reaction is arrested before the ketone is formed (p. 479).

If chloroformamide, $ClCO{\cdot}NH_2$, which is obtained by heating cyanuric acid in a current of hydrochloric acid gas, is passed into benzene containing aluminium chloride, benzamide is formed, which can be hydrolysed and converted into benzoic acid (p. 488)—

$$CONH + HCl = \underset{\text{Chloro.ormamide.}}{ClCO{\cdot}NH_2}.$$

$$C_6H_6 + ClCO{\cdot}NH_2[+ AlCl_3] = \underset{\text{Benzamide.}}{C_6H_5{\cdot}CO{\cdot}NH_2} + HCl.$$

Benzoic acid is manufactured on a large scale by passing the vapour of phthalic acid mixed with steam over a heated catalyst, when carbon dioxide is eliminated, and also from benzotrichloride by heating with milk of lime—

$$2C_6H_5{\cdot}CCl_3 + 4Ca(OH)_2 = \underset{\text{Calcium benzoate.}}{(C_6H_5COO)_2Ca} + 3CaCl_2 + 4H_2O.$$

The lime salt is decomposed by acid, and the benzoic acid crystallises out. It forms colourless needles, which melt at 121°–122° and boil at 250°. Benzoic acid is volatile in steam, and its vapours affect the throat and nose, producing coughing and sneezing. It is soluble in hot, but sparingly in cold water, and it dissolves in alcohol and ether. The insolubility of the majority of aromatic acids in water and their solubility in ether enable them to be separated and distinguished from many of the simpler aliphatic acids and hydroxy-acids. Benzoic acid forms well-defined salts. The calcium salt crystallises in long needles. Ferric benzoate is precipitated as a brown amorphous powder from neutral solutions with ferric chloride. The acid is separated and precipitated from the salts on the addition of hydrochloric acid.

Benzoyl Chloride, $C_6H_5{\cdot}COCl$, is prepared, like other acid chlorides, by the action of phosphorus tri- or penta-chloride on benzoic acid (p. 175)—

$$C_6H_5{\cdot}COOH + PCl_5 = \underset{\text{Benzoyl chloride.}}{C_6H_5{\cdot}COCl} + POCl_3 + HCl.$$

The product is fractionated, the benzoyl chloride being readily separated from the phosphorus oxychloride by reason of its higher boiling-point.

EXPT. 173.—Add a little benzoic acid to double its bulk of phosphorus pentachloride in a test-tube. The mixture becomes hot and liquefies, whilst clouds of hydrochloric acid fumes are evolved.

Benzoyl chloride is a colourless liquid which boils at 198° and fumes in moist air. It possesses the general characters of the aliphatic acid chlorides, and, like acetyl chloride, it combines with water, alcohols (though more slowly), and also with phenols, ammonia, and the amines (p. 177). These reactions are described in detail below.

Benzoic Anhydride, $C_6H_5CO{\cdot}O{\cdot}COC_6H_5$, is prepared, like acetic anhydride, by heating a mixture of benzoyl chloride and dry sodium benzoate. It is a crystalline compound which melts at 42°, and combines with phenols and alcohols like benzoyl chloride.

Benzamide, $C_6H_5{\cdot}CONH_2$, is readily obtained by adding ammonia or ammonium carbonate to benzoyl chloride, washing out the ammonium chloride with cold water, and crystallising from hot water the benzamide which is left—

$$C_6H_5{\cdot}COCl + 2NH_3 = \underset{\text{Benzamide.}}{C_6H_5{\cdot}CONH_2} + NH_4Cl.$$

EXPT. 174.—Add a few drops of strong ammonia solution to a drop of benzoyl chloride. There is a violent reaction, and a white deposit of benzamide and ammonium chloride is formed. Add a little water to dissolve the ammonium chloride, and crystallise the residue from hot water. The formation of benzanilide from aniline and benzoyl chloride may be shown in the same way.

Benzamide is also obtained, like acetamide, by heating ammonium benzoate in a sealed tube (p. 178), and by the Friedel-Crafts method described on p. 487. It is a colourless, crystalline substance which melts at 128°, and gives benzoic acid on hydrolysis like other amides.

Benzonitrile, *Phenyl cyanide,* $C_6H_5{\cdot}CN$, is prepared from aniline by Sandmeyer's reaction (p. 434), and from benzene sulphonic acid by fusion of the potassium salt with potassium cyanide (p. 451). A useful method of preparation is to distil benzoic acid with potassium, or lead sulphocyanide—

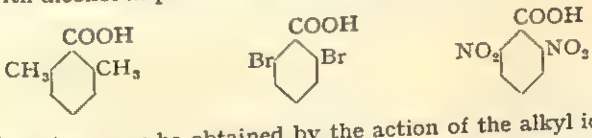
$$2C_6H_5COOH + KCNS = \underset{\text{Benzonitrile.}}{C_6H_5CN} + C_6H_5COOK + CO_2 + H_2S$$

Benzonitrile is a colourless liquid with a smell resembling nitrobenzene or benzaldehyde. It boils at 191°. On hydrolysis it yields benzoic acid.

Expt. 175.—Mix 3 c.c. of conc. sulphuric acid with 2 c.c. of water, add 1 gram of benzonitrile, and boil gently until complete solution is effected. On adding a little water and cooling, benzoic acid separates in needles.

Benzoic Esters.—The simplest method for obtaining the alkyl benzoates is that described in Expt. 65 (p. 185). Hydrochloric acid gas is passed into the alcohol until it has absorbed 4 to 5 per cent. by weight. It is boiled with benzoic acid. The product is poured into water, which is made alkaline to dissolve any unchanged benzoic acid, and the ester, which falls to the bottom as an oil, is removed and distilled.

Victor Meyer's Ester Law.—A reference has been made on p. 397 to the differences exhibited by the dimethyl derivatives of toluene on oxidation, and it was pointed out that the protective influence exercised by the proximity of certain groups, to the group submitted to the reaction, was not an uncommon occurrence. The most striking example of this protective influence is that afforded by the di-ortho-substituted benzoic acids. They cannot be converted into esters by the method just described, whereas a theoretical yield of the isomeric esters is obtained. The presence of methyl, nitro- and halogen groups in the two ortho-positions arrest esterification with equal effect. The following di-ortho-derivatives of benzoic acid form no esters when boiled with alcohol in presence of hydrochloric acid—



Yet the esters may be obtained by the action of the alkyl iodide on the silver salts. V. Meyer suggested that the ortho-substituents prevent access of the alcohol to the carboxyl group by reason of the space which they occupy, and called the effect *steric hindrance*. When the carboxyl group is moved farther away, as in substituted phenyl-acetic acid, there is no inhibiting effect. The indifference of di-ortho-esters of phenylcyanide, benzamide, and benzoic esters to the action of hydrolytic agents has also been attributed to steric hindrance, but it should be realised that whereas steric hindrance may be a controlling factor in some cases, there are many anomalies so that other causes may also have to be taken into account.

A simple and rapid method for preparing small quantities of esters, including phenolic esters, is that known as *Schotten-Baumann's reaction,* and consists in mixing the alcohol, or phenol, with benzoyl chloride, or other acid chloride, in presence of caustic soda solution—

$$C_6H_5{\cdot}COCl + C_2H_5OH + NaOH = \underset{\text{Ethyl benzoate.}}{C_6H_5CO{\cdot}OC_2H_5} + NaCl + H_2O.$$

The reaction is used to detect the presence of alcoholic or phenolic hydroxyl as well as of amino-groups, which form amides of the acid radical.

Expt. 176.—Mix together 1 c.c. of benzoyl chloride and 2 c.c. of ethyl alcohol, and add caustic soda solution until alkaline. Shake well and warm gently, keeping the liquid alkaline. The smell of the benzoyl chloride eventually disappears, and an oil with a fragrant smell collects at the bottom of the tube. This is ethyl benzoate. Repeat the reaction with phenol in place of ethyl alcohol. Solid phenyl benzoate is formed.

The alkyl benzoates are fragrant-smelling liquids which are specifically heavier than water (compare ethyl acetate). The methyl ester boils at 199°, the ethyl ester at 213°. The phenyl ester is a crystalline compound which melts at 71°.

Substituted Benzoic Acids.—Following the law of substitution (p. 412), the main product of the action of chlorine, bromine, sulphuric and nitric acids on benzoic acid is in each case the meta-compound. It should be noted, however, that with nitric acid all three isomeric nitro-compounds are formed, which yield amino-compounds on reduction. These amino-benzoic acids may be in turn diazotised and converted into the different derivatives to which the diazo-reaction gives rise. Another method for obtaining substituted benzoic acids is to oxidise the substituted toluene. For example, ortho- and para-chlorotoluene yield ortho- and para-chlorobenzoic acid, whilst direct chlorination of benzoic acid gives the meta-compound. In this way all three isomers may be obtained.

Methods may be readily devised for the preparation of most of the simpler substituted benzoic acids.

Anthranilic Acid, *o-Aminobenzoic acid,* $C_6H_4(NH_2){\cdot}COOH$, may be obtained by one of the methods described above; but in practice,

where large quantities are required for the manufacture of artificial indigo, it is produced from naphthalene. The process is described on p. 497. The methyl ester is the sweet-smelling constituent of the oil (neroli oil) extracted from orange blossom.

Saccharin, *Sulphobenzoimide*, $C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NH$, is obtained from toluene. The toluene on sulphonation forms a mixture of *p*- and *o*-sulphonic acid which is then converted into the sulphonic chloride. The ortho-compound, which is a liquid, is separated from the para-compound, which is a solid. From the ortho-compound the sulphon-amide is prepared. The latter is then oxidised to the corresponding benzoic acid derivative and on treatment with acid saccharin is formed.

$$\underset{\textit{o}\text{-Sulphonamide of benzoic acid.}}{C_6H_4\left\langle\begin{matrix}COOH\\SO_2NH_2\end{matrix}\right.} = \underset{\text{Saccharin.}}{C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NH} + H_2O.$$

Saccharin is a colourless, crystalline compound, which, when dissolved in water, has an intensely sweet taste, and is used in cases of diabetes and other disorders to replace cane-sugar in the patients' diet. Its sweetness is estimated at 400–500 times that of cane-sugar. A similar sweeting agent is prepared from naphthalene.

Toluic Acids, *Methylbenzoic acids*, $CH_3{\cdot}C_6H_4{\cdot}COOH$, exist in three isomeric forms, and are prepared by one or other of the general methods described under benzoic acid. They are crystalline substances resembling benzoic acid, and are readily identified by their melting-points. The ortho-acid melts at 103°, the meta-acid at 110°, and the para-acid at 180°. They yield the three phthalic acids on oxidation (p. 396).

Cumic Acid, *p-Isopropylbenzoic acid*, $C_3H_7{\cdot}C_6H_4{\cdot}COOH$, is prepared by the oxidation of cuminol (p. 477).

Phenolic Acids

Phenolic acids are derivatives of the aromatic acids in which one or more hydrogen atoms of the nucleus are replaced by hydroxyl. They combine the characters of phenols and acids. Many possess antiseptic properties, and give the colour reactions of the phenols with ferric chloride. They frequently occur among plant products, and many of them have found a technical application. Some of

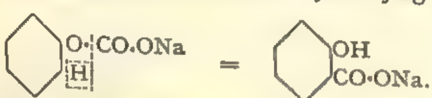
the amino-derivatives of hydroxy-esters are employed as local anæsthetics.

Salicylic Acid, *o-Hydroxybenzoic acid*, $C_6H_4(OH)\cdot COOH$, is found as the methyl ester, $C_6H_4(OH)\cdot COOCH_3$, in oil of winter-green, a fragrant liquid which is extracted from a heath (*Gaultheria procumbens*) grown in the United States and Canada. It is used for flavouring confectionery. It readily yields the acid on hydrolysis. A variety of synthetic methods exists for preparing salicylic acid, which a little reflection will suggest; but the manufacturing process, which is known as **Kolbe's reaction,** after its discoverer, is a peculiar one and unlike any previously described.

It consists in heating to 120°–130° dry sodium phenate with carbon dioxide in closed vessels under pressure. The process actually occurs in two steps. In the first reaction, sodium phenyl carbonate is formed—

$$C_6H_5ONa + CO_2 = \underset{\text{Sodium phenyl carbonate.}}{C_6H_5O\cdot CO\cdot ONa.}$$

Then, at the temperature of the reaction, an intramolecular change occurs, whereby the carboxyl group replaces hydrogen of the nucleus in the ortho-position to the hydroxyl group.



Sodium phenyl carbonate. Sodium salicylate.

It is an interesting fact that if potassium phenate is heated to 220° in carbon dioxide, the product is exclusively the para-compound, or if potassium salicylate is heated to the same temperature, it is converted into *p*-hydroxybenzoic acid.

Another method by which salicylic acid, together with *p*-hydroxybenzoic acid, is formed, is analogous to Reimer's reaction for preparing hydroxy-aldehydes (p. 480). A mixture of phenol, carbon tetrachloride, and caustic soda solution is heated together—

$$C_6H_5OH + CCl_4 + 6NaOH = C_6H_4\begin{cases} ONa \\ COONa \end{cases} + 4NaCl + 4H_2O.$$

The product, after removing excess of carbon tetrachloride, is saturated with carbon dioxide and shaken with ether to extract

unchanged phenol. The hydroxybenzoic acids are then precipitated with hydrochloric acid and filtered.

Salicylic acid crystallises in colourless needles, which melt at 155°. Its vapour has an irritating effect on the throat. It is very sparingly soluble in cold water, but dissolves readily in hot water. Like phenol and resorcinol, it gives an intense violet coloration with ferric chloride, and may be distinguished in this way from the isomeric meta- and para-compounds which give no colour reactions. On heating with soda-lime, salicylic acid loses carbon dioxide and is converted into phenol—

$$C_6H_4(OH)\cdot COOH = C_6H_5OH + CO_2.$$

EXPT. 177.—Grind up some salicylic acid, or its calcium salt, with double its bulk of soda-lime and heat over the flame. The smell of phenol is quickly detected.

Salicylic acid is a powerful antiseptic, and is frequently used as a substitute for phenol. **Salol,** the phenyl ester, and **betol,** the naphthyl ester (p. 542), of salicylic acid, are also used as antiseptics. They are obtained by the action of salicylic acid on phenol, or naphthol, in presence of an acid chloride (phosphorus oxychloride, or carbonyl chloride)—

$$C_6H_4(OH)COOH + C_6H_5OH = C_6H_4(OH)COOC_6H_5 + H_2O.$$

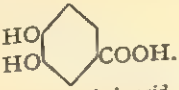
Salicylic acid is also an antipyretic and the sodium salt is used in cases of rheumatism. The acetyl derivative, *aspirin*,

$$C_6H_4(O\cdot COCH_3)\cdot COOH,$$

has a similar effect, but is less of an irritant.

Anisic Acid, *p-Methoxybenzoic acid*, $CH_3O\cdot C_6H_4\cdot COOH$, is obtained by the oxidation of anethole (p. 462). It is isomeric with methyl salicylate.

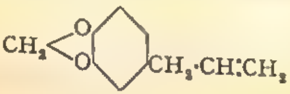
Protocatechuic Acid, $C_6H_3(OH)_2COOH + H_2O$, is one of six isomeric dihydroxybenzoic acids. It is a common constituent of aromatic compounds, which are present in certain resins, alkaloids, tannins, and yellow colouring matters associated with them. It has the following structure—



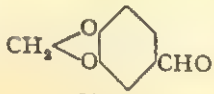
Protocatechuic acid.

It loses carbon dioxide, and is converted into catechol on heating. The tannins, which yield catechol on distillation, and are called catechol-tannins (see p. 496), probably contain protocatechuic acid as a constituent of the tannin molecule. Protocatechuic acid crystallises from water with one molecule of water of crystallisation, which it loses at 100°, and then melts at 199°. It gives a similar reaction to catechol with ferric chloride (p. 466), and like catechol reduces ammonia-silver nitrate but not Fehling's solution. The position of the groups in protocatechuic acid should be compared with those in vanillin and its allied compounds.

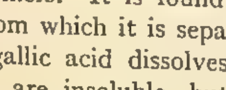
Piperonylic Acid is closely related to protocatechuic acid, not only in structure, but in its connection with the products of plant life. It may be termed methylene protocatechuic acid, and is readily converted into protocatechuic acid by heating with strong hydrochloric acid. **Piperonal** is the corresponding aldehyde, and is obtained by the oxidation of safrol (oil of sassafras). It has the scent of heliotrope, and is used as a perfume by the name of *heliotropin*. It bears the same relation to safrol that vanillin does to eugenol (p. 480).



Safrol.



Piperonal.



Piperonylic acid.

Gallic Acid, 1-2-3-5-*Trihydroxybenzoic acid*, $C_6H_2(OH)_3COOH$, is one of six possible isomers. It is found associated with certain tannins (see p. 495) from which it is separated by digestion with aqueous ether. The gallic acid dissolves in the ether, whereas the tannin substances are insoluble, but dissolve in the water present, and form a lower aqueous layer which can be separated. Gallic acid is also obtained by the hydrolysis of gallo-tannic, or digallic acid, which is the chief constituent of sumach and of galls, the round excrescences formed on oak leaves and twigs by the puncture of the gall-fly.

Gallic acid crystallises in colourless needles, which lose carbon dioxide on heating, forming pyrogallol (p. 468). It gives a deep blue coloration or precipitate with ferric chloride, and a pink

solution when shaken with potassium cyanide, which fades on standing, but reappears on shaking. In alkaline solution it rapidly darkens in the air by oxidation. It does not precipitate gelatine, and can by this means be distinguished from the tannins.

Ellagic Acid, $C_{14}H_8O_8$, is a substance closely related to gallic acid. It is frequently found associated with the tannins (in sumach) and may be obtained from gallic acid by oxidation with arsenic acid, or iodine. It is a yellow crystalline substance, which is insoluble in water and can therefore be readily separated from gallic acid and the tannins.

The Tannins.—This term is used for the active constituents of those substances which are used in tanning skins. The object of tanning is to prevent putrefactive changes, and to render the skin permanently flexible and porous. The hair is first removed from the skin, usually by the action of milk of lime, which at the same time causes the skin to swell. The lime is then dissolved out as far as possible by soaking the skins in fermenting dung, bran or old tan liquor, which contain organic acids (acetic, lactic, etc.) produced by fermentation. The skins are then steeped in tan liquor, which is the aqueous extract of a variety of vegetable substances, of which the following are among those commonly employed:—

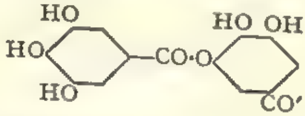
Oak bark.
Myrabolans (dried fruit of *Terminalia chebula*, India).
Valonia (acorn cup of *Quercus Ægilops*, Asia Minor).
Sumach (leaf of *Rhus coriaria*, Sicily).
Cutch (extract of wood of *Acacia catechu*, India).
Divi-divi (pod of *Cæsalpina coriaria*, S. America).
Hemlock bark (*Abies canadensis*, N. America).

Although the tannins differ widely in chemical constitution, and produce different effects on skins, they have the common property of precipitating gelatine from solution and forming insoluble compounds with it. It is this property, which is effective in producing leather; for the process of tanning has been successfully imitated by the use of formaldehyde, or inorganic compounds like chromic salts and alum, all of which render gelatine insoluble.

The tannins are astringent substances, which give dark blue or green colorations, or precipitates with ferric salts, and are precipitated by lead acetate, tartar emetic, and the alkaloids. The

use of tannin and tartar emetic as a mordant has been explained (p. 445). The tannins turn dark brown in presence of alkalis, and give a deep red coloration with potassium ferricyanide and ammonia. They are all very soluble in water, and insoluble in ether, but do not crystallise.

The tannins vary much in character, and little is known of their structure. Some appear to be glucosides of gallic acid, in which the hydroxyl groups of glucose are combined with gallic acid in the form of an ester, and decompose with acids into glucose and gallic acid; others appear to contain phloroglucinol in place of glucose, and protocatechuic acid in place of gallic acid. Tannic acid, from oak galls and sumach, decomposes into gallic acid and glucose on hydrolysis, and is probably a pentadigalloyl-glucose (Fischer). If the digalloyl group is represented by



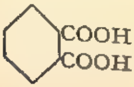
each of the five hydroxyl groups of glucose contains this radical in place of hydrogen.

A variety of synthetic tannins or "syntans" are produced by combining formaldehyde with a sulphonated phenol (phenol or cresol). These syntans are known by various names, such as *neradol*, *ordoval*, etc.

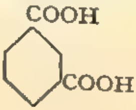
Quinic Acid, $C_6H_7(OH)_4 \cdot COOH$, already referred to (p. 481) as occurring in cinchona bark combined with the alkaloids, is the tetra-hydroxy-derivative of hexahydrobenzoic acid. It is a crystalline compound which melts at 162° and is optically active.

The Dibasic Acids

The most important dibasic acids are the three isomers, **phthalic, isophthalic,** and **terephthalic** acids, already mentioned as representing the final products of oxidation of the three isomeric xylenes :—



Phthalic acid.



Isophthalic acid.

Terephthalic acid.

The acids correspond to the aliphatic acids of the succinic acid series (p. 394) inasmuch as they form acid and neutral salts and esters.

Phthalic Acid, *Benzene-o-dicarboxylic acid*, $C_6H_4(COOH)_2$, is made in large quantities for the preparation of fluorescein and the eosin dyes (p. 525), and for conversion into anthranilic acid, now extensively used in the manufacture of artificial indigo (p. 529). It is also used for the manufacture of anthraquinone and dyes derived from it. It is obtained by oxidising naphthalene with air at 250° in presence of vanadium pentoxide. The product is converted into phthalic anhydride by sublimation—

$$\underset{\text{Naphthalene.}}{C_{10}H_8} + 9O = \underset{\text{Phthalic acid.}}{C_6H_4(COOH)_2} + 2CO_2 + H_2O.$$

$$C_6H_4(COOH)_2 = \underset{\text{Phthalic anhydride.}}{C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O} + H_2O.$$

The conversion of naphthalene into phthalic anhydride is adduced as affording valuable evidence of the structure of naphthalene, by indicating the probable existence in naphthalene of a benzene nucleus (p. 533).

In order to obtain anthranilic acid from phthalic anhydride, it is heated with ammonia, which converts it into phthalimide—

$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + NH_3 = \underset{\text{Phthalimide.}}{C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH} + H_2O.$$

Phthalimide is then warmed with bromine and potash, or potassium hypobromite. The alkali hydrolyses the phthalimide, yielding phthalaminic acid, and the subsequent reaction is the same as that by which acetamide is converted into methylamine (p. 206). The following scheme represents the series of changes—

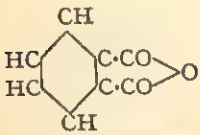
$$\underset{\text{Phthalimide.}}{C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH} \xrightarrow{H_2O} \underset{\text{Phthalaminic acid.}}{C_6H_4\left\langle\begin{matrix}CONH_2\\COOH\end{matrix}\right.}$$

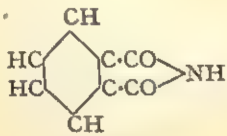
$$\xrightarrow{Br_2} C_6H_4\left\langle\begin{matrix}CON\vert HBr\\COOH\end{matrix}\right. \xrightarrow{KOH} C_6H_4\left\langle\begin{matrix}CON\\COOH\end{matrix}\right. \xrightarrow{H_2O} \underset{\text{Anthranilic acid.}}{C_6H_4\left\langle\begin{matrix}NH_2\\COOH.\end{matrix}\right.}$$

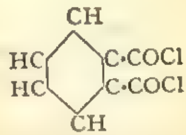
Intermediate products.

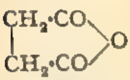
Phthalic acid, when heated quickly, melts at 213°, and at the same time passes into the anhydride.

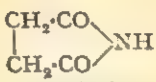
Phthalic Anhydride sublimes in long, colourless needles which melt at 128°. Heated with phenol and sulphuric acid, it gives *phenolphthalein* (p. 524); heated with resorcinol alone, *fluorescein* is formed (p. 525). The anhydride yields phthalimide with ammonia, and phthalyl chloride with phosphorus pentachloride. Each of these compounds has its representative among the derivatives of succinic acid (p. 349).

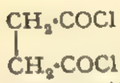

Phthalic anhydride.


Phthalimide.


Phthalyl chloride.[1]


Succinic anhydride,


Succinimide.


Succinyl chloride.

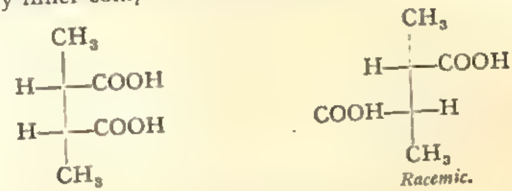
A much closer resemblance than that just described, subsists between dimethylsuccinic acid and hexahydrophthalic acid, which is obtained by the reduction of phthalic acid. Each of these acids exists in two stereoisomeric forms, and each of the isomers yields a different anhydride. The space arrangement of the isomers is represented in the diagram (p. 499), from which it will be seen that there are two asymmetric carbon atoms present as in tartaric acid, indicated in the diagram by the point of intersection of the cross lines. The two isomeric hexahydrophthalic acids correspond to the racemic and meso-forms, for they are both inactive; but as one of them has been resolved into its active components, this will represent the *trans* configuration. They are usually distinguished by the terms *cis* and *trans*; in the cis-compound the two carboxyl groups are close together, and in the trans-compound, diagonally opposite (p. 499).

If it is a question of asymmetry, the trans-compound in the diagram represents only one component of a racemic form (p. 369). The other

---

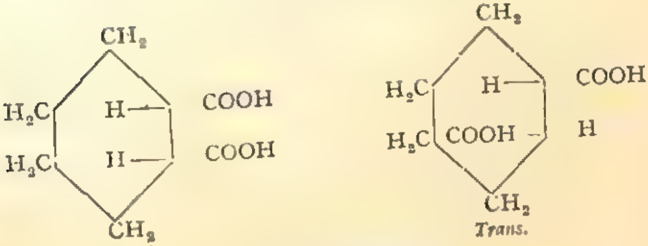
[1] It appears that phthalyl chloride can exist in a second form in which the two chlorine atoms are attached to the same carbon atom thus: $C_6H_4\langle\begin{smallmatrix}CCl_2\\ CO\end{smallmatrix}\rangle O$.

will be its mirror-image. The cis-compound is the meso-form, *i.e.* it is inactive by inner compensation (p. 369).



Meso. *Racemic.*

Dimethylsuccinic acids.



Cis. *Trans.*

Hexahydrophthalic acids.

Both hexahydroisophthalic and hexahydroterephthalic acids are represented by stereo-isomers.

Isophthalic Acid, *Benzene-m-dicarboxylic acid*, $C_6H_4(COOH)_2$, is prepared by a variety of synthetic processes. It is obtained from *m*-xylene, *m*-toluic acid, *m*-toluidine, etc. It is a crystalline substance, which melts above 300° and sublimes.

Terephthalic Acid, *Benzene-p-dicarboxylic acid*, $C_6H_4(COOH)_2$, is prepared by similar methods to those which yield the other two dibasic acids, *e.g.* from *p*-xylene, *p*-toluic acid, cuminol, and cymene, by oxidation, and further from *p*-toluidine and *p*-nitraniline. A little reflection, and a knowledge of the structure of the substances, will suggest the course of each reaction. Terephthalic acid sublimes on heating, but forms no anhydride.

Acids containing Carboxyl in the Side-Chain

These acids are the true representatives of the aliphatic acid among the benzene derivatives. They possess similar propertie and are prepared by similar methods. The analogy is furthe maintained in the system of nomenclature, which represents th

acid as a phenyl derivative of the corresponding aliphatic acid. A few examples will suffice.

Phenylacetic Acid, $C_6H_5{\cdot}CH_2{\cdot}COOH$, is prepared from benzyl chloride, which is first converted, by boiling with an aqueous-alcoholic solution of potassium cyanide, into benzyl cyanide. The product is fractionated, and the cyanide, which boils at 232°, is collected. The cyanide is finally hydrolysed with moderately strong sulphuric acid, when the phenylacetic acid crystallises—

$$\underset{\text{Benzyl chloride.}}{C_6H_5{\cdot}CH_2Cl} \longrightarrow \underset{\text{Benzyl cyanide.}}{C_6H_5{\cdot}CH_2CN} \longrightarrow \underset{\text{Phenylacetic acid.}}{C_6H_5{\cdot}CH_2{\cdot}COOH.}$$

Phenylacetic acid is a colourless, crystalline compound which melts at 76° and boils at 262°. When the acid is chlorinated or brominated by the direct action of the halogen, the halogen replaces the hydrogen of the α-carbon (the carbon atom next to the carboxyl group) of the side-chain as in the fatty acids (p. 153); in the cold it enters the nucleus. On oxidation benzoic acid is formed.

Mandelic Acid, *Phenylhydroxyacetic acid, Phenylglycollic acid,* $C_6H_5CH(OH){\cdot}COOH$.—Mandelic acid is isomeric with the hydroxy-toluic acids. It was originally prepared from amygdalin of bitter almonds by boiling with mineral acids. The benzaldehyde and hydrocyanic acid of the amygdalin, which are doubtless present in combination, are hydrolysed. The process has been imitated by forming the cyanhydrin of benzaldehyde, or mandelic nitrile (p. 475), and hydrolysing the product with strong hydrochloric acid.

$$\underset{\text{Mandelic nitrile.}}{C_6H_5CH(OH)CN} + 2H_2O = \underset{\text{Mandelic acid.}}{C_6H_5CH(OH){\cdot}COOH} + NH_3.$$

Mandelic acid bears a certain resemblance to lactic acid (p. 322). On oxidation with nitric acid, it yields benzoyl formic acid, and, on reduction with hydriodic acid, phenylacetic acid. Hydrochloric and hydrobromic acid give respectively chloro- and bromo-phenyl-acetic acid—

$$(HNO_3)\quad \underset{\text{Benzoyl formic acid.}}{C_6H_5{\cdot}CO{\cdot}COOH.} \qquad (HCl)\quad \underset{\text{Phenylchloracetic acid.}}{C_6H_5{\cdot}CHCl{\cdot}COOH.}$$

$$(HI)\quad \underset{\text{Phenylacetic acid.}}{C_6H_5{\cdot}CH_2{\cdot}COOH.} \qquad (HBr)\quad \underset{\text{Phenylbromacetic acid.}}{C_6H_5{\cdot}CHBr{\cdot}COOH.}$$

Like lactic acid, mandelic acid contains an asymmetric carbon atom, and exists in two optically active forms.

The acid of bitter almonds is lævo-rotatory; the synthetic product, which is necessarily inactive (p. 372), has been resolved into active components by fractional crystallisation of the salts of the active alkaloids, and also by sowing *penicillium* (green mould) in the solution of the ammonium salt, which destroys the lævo-acid and liberates the dextro-compound.

Mandelic acid melts at 133°. It dissolves in six times its weight of water at the ordinary temperature. Its solubility is such as might be anticipated from a hydroxy-acid.

Phenylpropionic Acid, *Hydrocinnamic acid,* $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is most conveniently obtained from cinnamic acid (see below) by reduction with sodium amalgam—

$$\underset{\text{Cinnamic acid.}}{C_6H_5{\cdot}CH{:}CH{\cdot}COOH} + H_2 = \underset{\text{Hydrocinnamic acid.}}{C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH.}$$

It crystallises in needles and melts at 47°.

Cinnamic Acid, *Phenylacrylic acid,* $C_6H_5{\cdot}CH{:}CH{\cdot}COOH$.—The acid is found as the benzyl ester in Peru and Tolu balsam (p. 472), in storax (p. 485), and in some gum-benzoins (p. 485). The usual method of preparation illustrates an important synthetic method, which is known as Perkin's reaction.

Perkin's reaction consists in heating together a mixture of an aldehyde (either aliphatic or aromatic), the sodium salt of a fatty acid and its anhydride, or some other anhydride. In the preparation of cinnamic acid, the materials are benzaldehyde, sodium acetate, and acetic anhydride, which are heated for several hours to 180°. Condensation occurs between the aldehyde and the fatty acid with the elimination of water, which is taken up by the anhydride. The anhydride is converted into the acid, which liberates the cinnamic acid from its sodium salt as follows—

$$C_6H_5CH\boxed{O + H_2}CH{\cdot}COONa = \underset{\text{Sodium cinnamate.}}{C_6H_5{\cdot}CH{:}CH{\cdot}COONa} + H_2O.$$

$$(CH_3CO)_2O + H_2O = 2CH_3{\cdot}COOH.$$

$$C_6H_5{\cdot}CH{:}CH{\cdot}COONa + CH_3{\cdot}COOH$$
$$= \underset{\text{Cinnamic acid.}}{C_6H_5{\cdot}CH{:}CH{\cdot}COOH} + CH_3{\cdot}COONa.$$

The cinnamic acid is separated from benzaldehyde by pouring the product into water, adding alkali, and distilling in steam. The benzaldehyde distils, and the cinnamic acid in the residual liquid is precipitated with hydrochloric acid, removed by filtration, and recrystallised from water.

Cinnamic acid forms colourless crystals which melt at 133°. It yields hydrocinnamic acid on reduction (p. 501) and benzaldehyde and benzoic acid by oxidation. The stereoisomer is known as *allocinnamic acid* (see p. 366).

Fittig's Researches.—The explanation of the course of Perkin's reaction, about which some difference of opinion at one time existed, is due to Fittig. He showed that the process is analogous to the formation of aldol (p. 134) and crotonaldehyde from acetaldehyde (p. 271).

The aldehyde first forms an additive compound with the acid, the carbon of the aldehyde group attaching itself to the α-carbon of the acid. A hydroxy-acid is formed, which is stable, if, as in isobutyric acid, the α-carbon has only one hydrogen atom attached. The process resembles the aldol condensation.

$$CH_3{\cdot}CHO + CH_3{\cdot}CHO = \underset{\text{Aldol.}}{CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO.}$$

$$C_6H_5{\cdot}CHO + \begin{array}{c}CH_3\\|\\CH{\cdot}COOH\\|\\CH_3\end{array} = C_6H_5{\cdot}CH(OH){\cdot}\begin{array}{c}CH_3\\|\\C{\cdot}COOH.\\|\\CH_3\end{array}$$

If, as in acetic and propionic acid, the group CH_2 is present in the α position, water is simultaneously removed and an unsaturated acid results. This process corresponds to the formation of crotonaldehyde (p. 271), or cinnamic aldehyde (p. 477).

$$CH_3{\cdot}CHO + CH_3{\cdot}CHO = CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO$$
$$= \underset{\text{Crotonaldehyde.}}{CH_3{\cdot}CH{:}CH{\cdot}CHO} + H_2O.$$

$$C_6H_5{\cdot}CHO + \begin{array}{c}CH_3\\|\\CH_2{\cdot}COOH\end{array} = \underset{\text{Intermediate compound.}}{C_6H_5{\cdot}CH(OH){\cdot}\begin{array}{c}CH_3\\|\\CH{\cdot}COOH\end{array}}$$

$$= \underset{\alpha\text{-Methylcinnamic acid.}}{C_6H_5{\cdot}CH{:}\begin{array}{c}CH_3\\|\\C{\cdot}COOH\end{array}} + H_2O.$$

It should be noted that the aldehyde carbon attaches itself always to the α-carbon atom, and that in the above reaction between benzaldehyde and propionic acid, phenylisocrotonic acid is not formed, as might be anticipated.

$$\underset{\text{Phenylisocrotonic acid.}}{C_6H_5{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH.}$$

Phenylisocrotonic acid can, however, be prepared by Perkin's reaction from benzaldehyde and succinic acid—

$$C_6H_5CHO + \overset{\displaystyle COOH}{\overset{|}{C}}H_2\cdot CH_2\cdot COOH = C_6H_5CH{:}CH\cdot CH_2\cdot COOH + CO_2 + H_2O.$$

From phenylisocrotonic acid, α-naphthol has been synthesised (p. 534).

Perkin's reaction and the formation of crotonaldehyde bear a close resemblance to Claisen's method for preparing cinnamic aldehyde. It is probable that in this, as in Perkin's reaction, the formation of a hydroxy-additive compound precedes that of the unsaturated product.

In reviewing these processes, it may be observed that the conditions of the reaction are determined by the presence of an aldehyde group on the one hand and a group $CH_2\cdot CO$ on the other. The general equation may be abbreviated in the following way—

$$\underset{\|}{C}O + \underset{|}{C}H_2\cdot \underset{|}{C}O = \underset{\|}{C}(OH)\cdot \underset{|}{C}H\cdot \underset{|}{C}O = \underset{\|}{C}{:}\underset{|}{C}\cdot \underset{|}{C}O + H_2O.$$

It is obvious that the number of unsaturated compounds of both the aromatic and aliphatic series may be multiplied almost indefinitely by means of these reactions. The unsaturated aromatic acids have the following properties in common. They form additive compounds with hydrogen, the halogen acids, and the halogens. On oxidation with alkaline permanganate in the cold, they take up two hydroxyl groups to form a dihydroxy-derivative, and, on further oxidation, ultimately divide at the double link. Cinnamic acid may be taken by way of illustration. On reduction it forms phenylpropionic acid; with hydrobromic acid, phenyl-β-bromopropionic acid (the bromine attaches itself to the β-carbon, see p. 270); with bromine, phenyl-αβ-dibromopropionic acid; on oxidation with permanganate, phenylglyceric acid, and then benzaldehyde and benzoic acid—

(H_2)	$C_6H_5\cdot CH_2\cdot CH_2\cdot COOH$. Phenylpropionic acid.
(HBr)	$C_6H_5\cdot CHBr\cdot CH_2\cdot COOH$. Phenyl-β-bromopropionic acid.
(Br_2)	$C_6H_5\cdot CHBr\cdot CHBr\cdot COOH$. Phenyl-αβ-dibromopropionic acid.
$(H_2O + O)$	$C_6H_5\cdot CH(OH)\cdot CH(OH)\cdot COOH$. Phenylglyceric acid.

The above reactions should be compared with those of ethylene and acrylic acid.

αβ and βγ Unsaturated Acids.—These two kinds of unsaturated acids are represented by cinnamic and phenylisocrotonic acid, and are denoted by the position of the double bond which lies between the α

and β carbon atoms in cinnamic acid and the β and γ carbon atoms in phenylisocrotonic acid.

An interesting relation exists between the two groups of acids. It has been found that, on heating $\beta\gamma$-acids with caustic soda solution, a shifting of the double link to the $\alpha\beta$-position takes place—

$$\underset{\gamma}{C_6H_5CH}\text{:}\underset{\beta}{CH}\cdot\underset{\alpha}{CH_2}COOH = C_6H_5\underset{\gamma}{CH_2}\cdot\underset{\beta}{CH}\text{:}\underset{\alpha}{CH}\cdot COOH.$$

The behaviour of these acids has played an important *rôle* in the study of chemical structure.

***o*-Nitrophenylpropiolic Acid,** $C_6H_4(NO_2)\cdot C\vdots C\cdot COOH$.—This acid is readily converted into indigo-blue (p. 529), and was at one time manufactured as a source of the dye. It is obtained from cinnamic acid by nitration. Ortho- and para-nitrocinnamic acids are formed together, and are separated by conversion into the ethyl esters, which have very different solubilities in alcohol, the para-compound being very sparingly, the ortho-compound easily soluble. The ester is then hydrolysed and the free acid brominated. By treatment with strong caustic potash in the cold, *o*-nitrophenylpropiolic acid is obtained—

$$C_6H_5\cdot CH\text{:}CH\cdot COOH + HNO_3 = \underset{\text{Nitrocinnamic acid.}}{C_6H_4(NO_2)CH\text{:}CH\cdot COOH.}$$

$$C_6H_4(NO_2)\cdot CH\text{:}CH\cdot COOH + Br_2 = \underset{o\text{-Nitrophenyl-}\alpha\beta\text{-dibromopropionic acid.}}{C_6H_4(NO_2)CHBr\cdot CHBr\cdot COOH.}$$

$$C_6H_4(NO_2)CHBr\cdot CHBr\cdot COOH + 2KOH$$
$$= \underset{o\text{-Nitrophenylpropiolic acid.}}{C_6H_4(NO_2)C\vdots C\cdot COOH} + 2KBr + 2H_2O.$$

It is a crystalline compound which melts at 156°. On warming with alkalis in presence of grape-sugar it is converted into indigo (p. 529).

Coumarin, $C_6H_4\left\langle\begin{array}{l}CH\text{:}CH\\ \quad\quad\;|\\ O\text{—}CO\end{array}\right.$, is the lactone, or inner ester, of *o*-hydroxycinnamic acid. It is the sweet-smelling constituent of woodruff, the tonka bean, and new-mown hay. It is prepared from salicylaldehyde (p. 479), by the same process by which cinnamic acid is obtained from benzaldehyde. The hydroxy-cinnamic acid, which is formed, passes spontaneously into the lactone, when liberated from its sodium salt.

It is a colourless, crystalline compound, which melts at 67° and has a pleasant aroma.

Questions on Chapter XXXIV.

1. How may benzoic acid be prepared from each of the following substances: benzene, toluene, phenylcyanide, benzaldehyde, and benzyl alcohol? Which of these methods is of general application, and might be employed for the preparation of acetic acid?

2. Compare the physical and chemical properties of the aliphatic and aromatic acids by reference to acetic and benzoic acid.

3. Describe the preparation of benzoyl chloride and the action upon it of (1) ammonia, (2) aniline, (3) alcohol, (4) sodium benzoate. Give equations.

4. Describe a common method for obtaining benzoic esters. Does the preparation of the derivatives of benzoic ester offer any difficulty?

5. How can *o*-chlorobenzoic acid be obtained from *o*-chloronitrobenzene, *m*-chlorobenzoic acid from benzoic acid, and *p*-chlorobenzoic acid from *p*-chlorotoluene?

6. What is anthranilic acid? How may it be converted into salicylic and *o*-chlorobenzoic acid?

7. Describe the preparation of *saccharin* from toluene. What is its chemical name, and for what purpose is it used?

8. Explain *Kolbe's reaction* by reference to the synthesis of salicylic acid. Mention any reactions by which salicylic acid may be identified and distinguished from the *m*- and *p*-hydroxy-benzoic acids. How is salicylic acid converted into phenol, benzene, and benzoic acid?

9. Explain the structural relations which exist between protocatechuic acid, vanillin, and piperonylic acid.

10. How is gallic acid obtained? Name those reactions by which it is distinguished from gallotannic acid on the one hand and pyrogallol on the other.

11. Give an account of the *tannins* and their use in the preparation of leather. Name some tannin-containing products.

12. Describe the preparation of phthalic acid from naphthalene, isophthalic acid from *m*-xylene, and terephthalic acid from *p*-toluidine. How can these three acids be distinguished?

13. Compare phthalic and succinic acids.

14. How is phthalic acid prepared? Describe its constitution and state how it may be transformed into benzoic acid and benzene.

15. In what manner do mandelic and lactic acids resemble one another?

16. Describe and explain *Perkin's reaction*. How are isomeric compounds of the formula $C_6H_5{\cdot}C_3H_4{\cdot}COOH$ obtained? By what characteristic properties are they distinguished? Draw a comparison between Perkin's and Claisen's reactions.

17. Give examples of the application of Perkin's reaction to the preparation of coumaric and *o*-nitrophenylpropiolic acids.

CHAPTER XXXV

THE TERPENES AND CAMPHORS

THE fragrant oils which occur in flowers, fruits, leaves, and stems of plants are grouped together under the name of **essential oils** in order to distinguish them from the fixed oils and fats. The essential oils are volatile with steam and comprise a large number of products of different kinds used in pharmacy and perfumery. Among them occur, chiefly in the *coniferae* and *citrus* families, a number of unsaturated hydrocarbons called **terpenes,** with the empirical formula C_5H_8. The *terpenes proper* have the molecular formula $C_{10}H_{16}$, and are cyclic compounds derived by partial reduction from *p*-cymene (p. 398). The effect of this reduction is to render the cyclic nucleus unsaturated in character. The *monocyclic terpenes* possess two olefinic bonds and two side-chains; the *bicyclic terpenes* have only one double bond, but two ring structures, since the 6-membered ring is bridged by the attachment of the isopropyl group to a second point, as in pinene. In addition to the terpenes proper are the *sesquiterpenes*, $C_{15}H_{24}$, the *polyterpenes*, $(C_5H_8)_n$, and the open-chain olefine, **isoprene,** C_5H_8, which is obtained by the dry distillation of rubber, and is apparently the parent substance of other terpenes which may all be regarded as polymers of isoprene. The **camphors** are derivatives of terpenes containing oxygen, and are mostly alcohols, aldehydes or ketones. Among the more important members of the group of terpenes and camphors are *pinene*, *limonene*, *terpineol*, *menthol*, *borneol*, *camphor*, and the olefinic terpene aldehyde *geranial* or *citral*, which are described below.

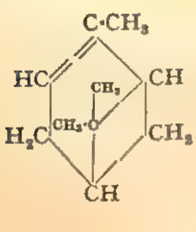
Pinene, $C_{10}H_{16}$, is the chief constituent of oil of turpentine. It is obtained from rosin, the exudation from the stems of conifers, by distillation with water. It is also present in varying quantities in many of the essential oils. It boils at 155°, and has a specific

gravity of 0·858. Pinene is found in two optically active forms: the dextro-compound, or *australene*, is contained in American turpentine (*Pinus australis*); the lævo-compound, or *terebenthene*, in French turpentine (*Pinus maritima*). When hydrochloric acid gas is passed into pinene, a solid crystalline compound, pinene hydrochloride, sometimes termed *artificial camphor*, $C_{10}H_{16}{\cdot}HCl$, is formed. With iodine or sulphuric acid, pinene is converted into cymene (p. 399). Its constitution is fully established.

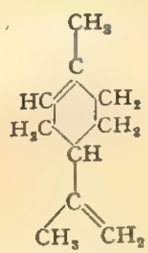
Turpentine oil is used as a solvent in the preparation of varnishes, for mixing with pigments, as an embrocation, etc. It absorbs oxygen, when heated in presence of water, and the oxygenated water is employed as a disinfectant and deodoriser.

Limonene, $C_{10}H_{16}$, is one of the constituents of oil of lemons, limes, citrons, etc., and is extracted from the rind. Like pinene, it is optically active, and is found in dextro- and lævo-forms. *Dipentene* is the inactive racemic form, and its properties differ somewhat from those of the limonenes. It is obtained by mixing together equal quantities of the two active limonenes; but it is also frequently found in different essential oils, and in turpentine. Dipentene has been obtained synthetically.

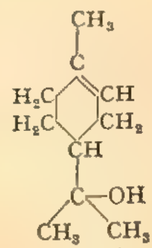
Limonene boils at 175°, and has a specific gravity of 0·846. It combines with 2 molecules of the halogens and halogen acids, and forms crystalline additive compounds of the formulæ $C_{10}H_{16}Br_4$, $C_{10}H_{18}Br_2$, which are explained by the presence of two double bonds in the molecule. The structures of pinene, limonene (dipentene) and terpineol are represented thus—



Pinene.



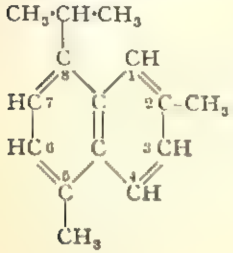
Limonene (Dipentene).

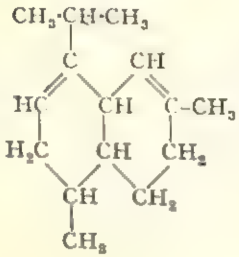


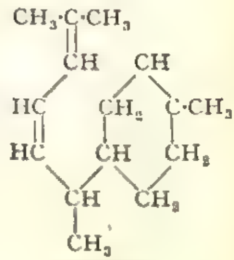
Terpineol.

The Sesquiterpenes, $C_{15}H_{24}$, are very numerous, and are related to the aromatic hydrocarbon *cadalene* or 2 : 5-dimethyl 8-isopropyl

naphthalene in much the same way as the terpenes proper are related to *p*-cymene. *Cadinene*, from oil of cubebs, contains two double bonds in the condensed ring system, while *zingiberene*, from oil of ginger, and *bisabolene*, from myrrh and bergamot oil, are both monocyclic, the bond between carbon atom 8 and the other ring being severed—

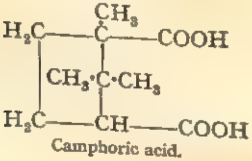

Cadalene.

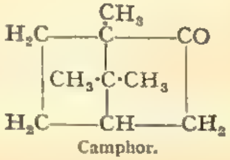

Cadinene.


Zingiberine.

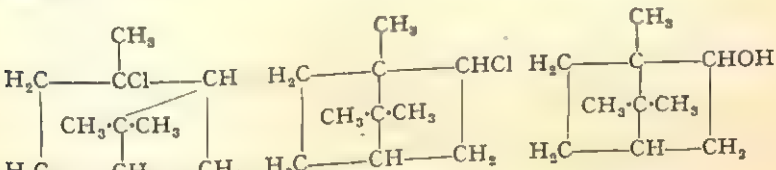
Camphor, $C_{10}H_{16}O$, is obtained from the camphor tree (*Laurus camphora*) by boiling the wood with water in a vessel covered with a perforated dome, into which the camphor sublimes. It is a colourless, crystalline substance, with a characteristic smell. It melts at 175°, and boils at 204°. In spite of its high melting- and boiling-points, it vaporises appreciably at ordinary temperatures. Ordinary or Japan camphor is dextro-rotatory; matricaria camphor (*Matricaria parthenium*) is lævo-rotatory. Camphor is a ketone, for it gives an oxime, *camphoroxime*, $C_{10}H_{16}$:NOH, with hydroxylamine, and a secondary alcohol, *borneol*, $C_{10}H_{17}(OH)$, on reduction. When oxidised with nitric acid, it yields *camphoric acid*, $C_8H_{14}(COOH)_2$, which is a dibasic acid. When distilled with phosphorus pentoxide, or pentasulphide, it forms cymene.

Both camphoric acid and camphor have been synthesised and their formulæ are well established.


Camphoric acid.


Camphor.

When hydrogen chloride acts upon pinene at a low temperature an addition product, pinene hydrochloride, $C_{10}H_{16}\cdot HCl$, is formed, which isomerises to *bornyl chloride*, a substance strongly resembling natural camphor in smell, and known as *artificial camphor*. This change involves a structural rearrangement from the meta-bridging of pinene to the para-bridging which occurs in camphor. The hydrogen chloride can be removed by lime, but the resulting product is not pinene, but an isomer called *camphene*. Like pinene, camphene also combines with hydrogen chloride, and camphene hydrochloride isomerises to *isobornyl chloride*, a geometrical isomeride of bornyl chloride. On hydrolysis bornyl and isobornyl chlorides yield the secondary alcohols *borneol* and *isoborneol*, both of which can be oxidised to the ketone camphor. This synthetic camphor differs from the natural product in being optically inactive.

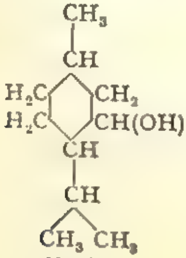


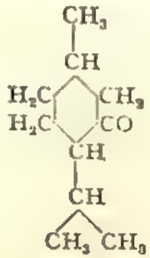
Pinene hydrochloride. Bornyl and isobornyl hydrochloride. Borneol and isoborneol.

Borneol, *Borneo camphor*, $C_{10}H_{17}(OH)$, is found in Nature in the dextro-, lævo-, and inactive forms. The common or Borneo camphor, which is dextro-rotatory, is obtained from a tree, *Dryobalanops camphora*, growing in Borneo and Sumatra. It is a crystalline compound, which melts at 203° and boils at 212°. It is prepared from camphor by reduction with sodium in alcoholic solution, which gives *isoborneol* at the same time.

Menthol, $C_{10}H_{19}(OH)$, is the chief constituent of peppermint oil, to which it lends the characteristic smell. It is the crystalline residue left on distillation, after removal of the terpenes. It is a colourless, crystalline substance, which melts at 42° and boils at 212°. It is a secondary alcohol, and yields the ketone, *menthone*, $C_{10}H_{18}O$, on oxidation, and *menthyl chloride*, $C_{10}H_{19}Cl$, by the

action of phosphorus pentachloride. It is lævorotatory; the racemic form can be made by reducing thymol (p. 465).

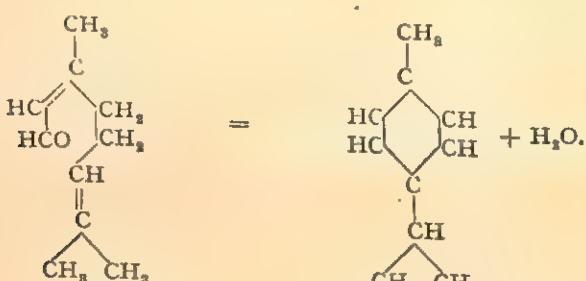

Menthol.


Menthone.

Olefinic Terpenes and Camphors.—These substances are associated with the terpenes and camphors in essential oils, and are closely related to them chemically, although they strictly belong to the aliphatic series. The olefinic terpenes have acquired in recent years a special interest, from the discovery of their value as perfumes. They constitute the true perfume of many essential oils.

The scent of geranium oil, oil of lemons, lavender, bergamot, coriander, linaloes, and attar of roses is derived from these substances. Two examples will be given.

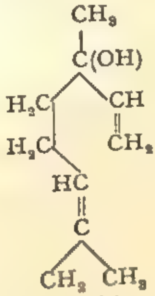
Geranial, *Citral,* $C_{10}H_{16}O$, is isomeric with camphor. It is an aldehyde, which gives on reduction the alcohol, *geraniol.* It is readily converted into cymene by heating with potassium hydrogen sulphate—


Geranial. Cymene.

Geranial is present in lemon-grass oil, oil of lemons, and in citron oil; geraniol gives the perfume to rose oil, oil of lavender, ylang

ylang, and many other essences. It is converted into linalol when heated with steam under pressure.

Linalol, $C_{10}H_{18}O$, is an alcohol which has the following structural formula—



Linalol.

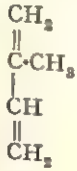
It is found, occasionally with linalyl acetate, in linalol oil, in bergamot, coriander, and lavender oils. Heated with formic acid it is converted into dipentene.

Caoutchouc (rubber) and **Gutta-percha** are hydrocarbons of the formula $(C_5H_8)_n$ which are closely related to the terpenes. They are extracted as viscid emulsions (*latex*) by making incisions into the bark of certain trees (gutta percha from trees of the order of *Sapotaceæ* found in the Malay Peninsula and rubber from *Hevea brasiliensis, manihot,* etc., cultivated in Brazil, Ceylon, and other tropical countries). The emulsion coagulates on standing, or more rapidly on heating and is the source of the well-known materials found in trade. The natural rubber is usually treated with sulphur or sulphur compounds with which it combines and then retains its elastic properties for a longer period. Rubber appears to be a polymeride of the hydrocarbon, *isoprene*: for rubber on distillation yields this compound, and substances similar to rubber have been obtained synthetically by polymerisation of unsaturated hydrocarbons such as isoprene and butadiene [1] in presence of metallic sodium or other catalyst.

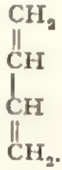
The structure of rubber is still undetermined, being regarded by

[1] The termination "ene" indicates an unsaturated hydrocarbon group as in ethylene; the termination "diene" represents two such hydrocarbon groups, and so forth. Isoprene might be termed methyl butadiene (p. 255).

some as a chain of indeterminate length of isoprene groups and others as such groups combined into a ring.



Isoprene.



Butadiene.

Questions on Chapter XXXV

1. Give a general account of the constituents of the essential oils.

2. Explain the relationship of the following: pinene, camphor, and cymene. What are the chief sources of pinene and camphor, and how are they obtained?

3. From the formula of limonene, explain the existence of two optically active forms. What relation do they hold to dipentene? What are the sources of limonene?

4. Why is camphor regarded as a ketone? What is its relation to borneol?

5. Explain the formation of menthyl chloride and menthone from menthol.

6. Give a short account of the olefinic terpenes and camphors. Why are they classed among the terpenes and camphors? What relation do they bear to cymene and the terpenes?

CHAPTER XXXVI

MULTINUCLEAR HYDROCARBONS AND THEIR DERIVATIVES

Multinuclear Hydrocarbons are formed by the linking together of two or more benzene nuclei. The simplest example is **diphenyl,** in which the carbon atoms of two benzene nuclei are united, or, in other words, a hydrogen atom of benzene is replaced by phenyl. Theoretically, each hydrogen of the nucleus might be so replaced, and each new nucleus might be the centre of a new series of phenyl derivatives. In reality, the number of such compounds is small, and is limited to two isomeric diphenyl- and two isomeric triphenyl-benzenes.

$C_6H_5 \cdot C_6H_5$.	$C_6H_4(C_6H_5)_2$.	$C_6H_3(C_6H_5)_3$.
Diphenyl.	Diphenylbenzene.	Triphenylbenzene.

Again, the phenyl groups, instead of being directly linked, may be united by one or more carbon atoms. Diphenyl- and triphenyl-methane and dibenzyl are well-known instances.

$C_6H_5 \cdot CH_2 \cdot C_6H_5$.	$(C_6H_5)_3CH$.	$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$.
Diphenylmethane.	Triphenylmethane.	Dibenzyl, or Diphenylethane.

It is unnecessary to multiply examples. We shall confine our attention to the better known members of the group, which form the basis of important colouring matters.

Diphenyl, $C_6H_5 \cdot C_6H_5$, is found in small quantities in coal-tar. It may be prepared by passing benzene through a red-hot tube, or by Fittig's method by acting upon bromobenzene with sodium.

Diphenyl is a colourless, crystalline substance, which melts at 71° and boils at 254°. In its behaviour with nitric and sulphuric acids and the halogens it resembles benzene. The only derivative of importance is diaminodiphenyl or benzidine, which may be obtained by the reduction of dinitrodiphenyl, but is more readily prepared from nitrobenzene (see below).

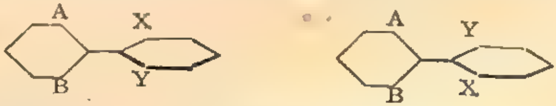
Benzidine, *p-Diaminodiphenyl,* $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2$.—The manufacturing process for obtaining benzidine is by the reduction

in alkaline solution of nitrobenzene to hydrazobenzene. The hydrazobenzene is then boiled with strong hydrochloric acid and converted into benzidine (p. 442). Or, azobenzene may be first prepared, and by reducing it in acid solution, converted into hydrazobenzene, which is changed by the acid into benzidine.

Tolidine, *Diaminoditolyl*, is prepared in the same way from *o*- and *m*-nitrotoluene. The para-compound cannot be obtained by this method, for it is the carbon atom in the para-position to the amino-group which serves as the link between the two nuclei and in *p*-nitrotoluene the position is already appropriated.

Benzidine and *o*-tolidine have already been referred to as forming important azo-dyes, which are known as Congo reds and benzopurpurins (p. 445).

A further interest attaching to diphenyl derivatives is the existence of optically active forms, not due in this case to the presence of asymmetric carbon, but to the restricted rotation of the two attached benzene rings. If the groups attached to the rings prevent their free rotation they may have different configurations which correspond to object and image, in other words, the molecule as a whole is unsymmetrical and is therefore capable of existing in optically active forms. Representing by models the two rings in planes at right angles and the restricting groups by A, B and X, Y, it will be seen that the two models do not overlap.



Diphenylmethane, $C_6H_5{\cdot}CH_2{\cdot}C_6H_5$, is most readily obtained from benzyl chloride and benzene in presence of aluminium chloride or the aluminium-mercury couple—

$$C_6H_5CH_2Cl + C_6H_6 = \underset{\text{Diphenylmethane.}}{C_6H_5{\cdot}CH_2{\cdot}C_6H_5} + HCl.$$

It has a pleasant smell; it melts at 26° and boils at 263°. When oxidised it yields benzophenone. The reaction is without analogy among the paraffins, and must be ascribed in the case of diphenylmethane to the influence of the benzene nuclei, just as the presence of hydroxyl in the alcohols facilitates the further replacement of hydrogen by oxygen. Benzophenone by the reverse process of reductions forms diphenylmethane (p. 479).

Triphenylmethane, $CH(C_6H_5)_3$, is the mother substance of a great variety of dyes, which are generally included under the name of *triphenylmethane colours.*

Triphenylmethane itself is a colourless, crystalline compound, which melts at 92°, and forms a molecular compound with one molecule of benzene, melting at 75°. It is obtained by the action of aluminium chloride on a mixture of chloroform and benzene by the ordinary process of Friedel and Crafts.

$$CHCl_3 + 3C_6H_6\ [+ AlCl_3] = \underset{\text{Triphenylmethane.}}{CH(C_6H_5)_3} + 3HCl.$$

On oxidation it yields triphenylcarbinol, $(OH)C(C_6H_5)_3$, which appears to possess the properties of a weak base, and may be termed triphenyl carbonium hydroxide, for it forms an unstable chloride and sulphate with hydrochloric and sulphuric acids (p. 236)—

$$\underset{\text{Triphenylmethyl chloride.}}{(C_6H_5)_3C{\cdot}Cl.} \qquad \underset{\text{Triphenylmethyl sulphate.}}{(C_6H_5)_3C{\cdot}SO_4H.}$$

By the action of finely divided silver on triphenylmethyl chloride in benzene solution a colourless, crystalline compound is obtained on evaporation of the solvent having the composition of hexaphenyl ethane, $(C_6H_5)_3C{\cdot}C(C_6H_5)_3$, but possessing very unusual properties. Though colourless in the solid form, it dissolves in organic solvents with a yellow colour and absorbs oxygen with avidity forming a peroxide, $(C_6H_5)_3C{\cdot}O{\cdot}O{\cdot}C(C_6H_5)_3$, and combining with halogens to form triphenylmethyl halides. Determinations of the molecular weight in the solution and other properties indicate the presence of tervalent carbon as *triphenyl methyl,* $(C_6H_5)_3C$.

Colour and Structure.—It has already been stated (p. 446) that the azo-group is a chromophor forming a part of the chromogen, azobenzene, which is a highly coloured substance. According to the theory of Witt the following unsaturated groups may also act as chromophors—

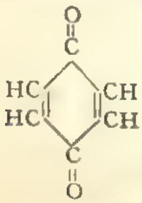
$$C{=}C;\ C{=}O;\ C{=}N;\ N{<}^{O}_{O};\ \text{and } N{=}O,$$

and when they enter into a compound form a chromogen, which may or may not be coloured. The manifestation of colour is usually associated with one or more aromatic nuclei, and, according to one view, is due to the reduplication of double linkages; according to another it is due to the selective absorption of the aromatic nucleus. The colour of a substance arises from its power of absorbing certain of the light rays of the visible spectrum and reflecting others.

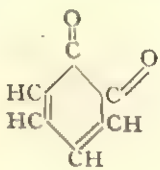
Solutions of coloured substances placed in the path of a beam, which is refracted through the prism of a spectroscope, show a series of absorption bands. Benzene, though it does not absorb in the visible spectrum, shows bands in the ultra-violet (or that portion of the invisible spectrum lying beyond the violet) and which, though it does not affect the eye, will affect a photographic plate. These bands of benzene lie on the border of the visible spectrum and the effect of the chromophor is to slow down the vibrations and thus shift the absorption to the visible region, which then manifests itself as colour. Thus, the single chromophor CO in benzophenone produces a colourless product; but the diketone, benzil, is yellow, and the triketone is orange.

Benzophenone .	$C_6H_5 \cdot CO \cdot C_6H_5$	colourless
Benzil . . .	$C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$	yellow
Diphenyltriketone	$C_6H_5 \cdot CO \cdot CO \cdot CO \cdot C_6H_5$	orange

The same applies to ortho- and para-benzoquinone, in which the ketone groups are associated with two pairs of double bonds; the ortho-compound, in which the ketone groups reinforce one another, is the more deeply coloured.



Yellow.



Orange.

In certain classes of dyes, which are basic or acid, it is found that the substances themselves are colourless, and that the colour is only produced on their conversion into salts; that others again change their colour. These changes are usually explained by a change of structure, in which an arrangement of double bonds similar to that in quinone, known as a *quinonoid structure*, is supposed to take place. We shall see presently that the free base of malachite green, magenta and other basic dyes are colourless, and only their salts are coloured. Again, aminoazobenzene (p. 438) is orange in colour, but its salts are violet. The change is again accompanied by a change of structure.

Aminoazobenzene .	$NH_2 \cdot C_6H_4N{=}N \cdot C_6H_5$	orange
Hydrochloride . .	$HCl \cdot NH{=}C_6H_4{=}N \cdot NHC_6H_5$	violet

A similar kind of change is supposed to occur when colourless *p*-nitrophenol is dissolved in caustic soda solution—

Colourless *p*-Nitrophenol. Orange Sodium nitrophenate.

Malachite green, *Benzaldehyde green,* is one of the simplest of the triphenylmethane colours. The first step in its preparation is to heat together a mixture of benzaldehyde (1 mol.), dimethylaniline (2 mols.), and solid zinc chloride. The benzaldehyde and dimethylaniline combine with the elimination of a molecule of water, which is absorbed by the zinc chloride. The product, tetramethyldiaminotriphenylmethane, is a colourless, crystalline substance, which is usually called the *leuco-base* of malachite green, and is insoluble in water. Its formation is represented as follows—

$$\begin{array}{l} C_6H_5 \\ HC\,O + \begin{array}{l} H\,C_6H_4N(CH_3)_2 \\ H\,C_6H_4N(CH_3)_2 \end{array} \end{array} = HC\begin{cases} C_6H_5 \\ C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2 \end{cases} + H_2O.$$

Leuco-base of Malachite green.

The second step is to oxidise the leuco-base by means of lead peroxide and hydrochloric acid. The triphenylmethane derivative is converted into the carbinol, or base of malachite green, which, like the leuco-base, is a colourless substance, insoluble in water; but, in the presence of the acid, it forms the soluble chloride, which constitutes the dye.

Expt. 178.—Dissolve a little of the leuco-base in very dilute hydrochloric acid, add a minute quantity of lead peroxide, shake up for a minute, and pour into a large volume of water.

These changes are represented as follows—

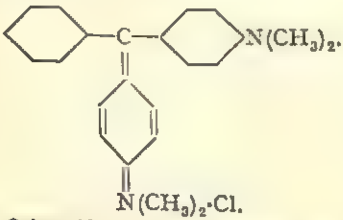
$$HC\begin{cases} C_6H_5 \\ C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2 \end{cases} \xrightarrow{O} (HO)C\begin{cases} C_6H_5 \\ C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2. \end{cases}$$

Leuco-base of Malachite green. Base of Malachite green.

$$\xrightarrow{HCl} Cl\cdot C\begin{cases} C_6H_5 \\ C_6H_4N(CH_3)_2. \\ C_6H_4N(CH_3)_2 \end{cases}$$

Malachite green.

The constitution of the salts of malachite green is at present undetermined. The general consensus of opinion is in favour of what is termed a *quinonoid* structure for many colouring matters; that is, a structure containing one or more double links of the kind that occur in quinone between carbon and oxygen. The quinonoid structure for malachite green is represented as follows—



Quinonoid structure of Malachite green.

In this formula the only position available for the acid radical in the salts is with the doubly-linked nitrogen atom, which becomes thereby quinquevalent.

Rosaniline, *Magenta, Fuchsine,* was one of the earliest of the synthetic dyes, and was originally obtained by oxidising with arsenic acid a mixture of aniline, *o*- and *p*-toluidine.

Expt. 179.—Mix together in a boiling tube about 2 grams each of aniline, *o*- and *p*-toluidine with twice the weight (12 grams) of syrupy arsenic acid, and heat the mixture in a fusible-metal bath to 180°–190° for half an hour. The product, which is the arsenate of rosaniline, dissolves in water with a bright magenta colour.

When the product is extracted with water and treated with common salt, the rosaniline, which is present as the arsenate, is converted into the hydrochloride of rosaniline, and, on evaporation, green, iridescent crystals are deposited.

To avoid the use of arsenic in the preparation, nitrobenzene is used in its place together with hydrochloric acid and iron filings. The oxidising agent is the nitrobenzene, and the ferrous chloride, which is formed when the iron dissolves in the hydrochloric acid, acts as carrier, becoming alternately oxidised to ferric and reduced to ferrous salt.

Rosaniline base is, when pure, a colourless substance like the base of malachite green, and is precipitated from a solution of magenta by the addition of ammonia.

EXPT. 180.—Dissolve a few crystals of magenta in water, and whilst carbon dioxide is passing through the solution add ammonia. Magenta base is precipitated in a nearly colourless form. If a skein of wet wool or silk is steeped in the colourless liquid, it takes up the colour and is dyed, showing that a salt of the base is formed with a constituent of the fibre.

It dissolves in strong hydrochloric acid with a brown colour, which changes to magenta on pouring into water. When sulphur dioxide is passed through a solution of magenta, the colour vanishes owing to the formation of the hydrochloride of the colourless leuco-base.

Para-rosaniline is prepared, like rosaniline, from a mixture containing, however, only aniline and *p*-toluidine. More important is the synthesis from triphenylmethane, which, in the skilful hands of E. and O. Fischer, served the double purpose of explaining the structure of magenta and the course of the reaction by which it is obtained.

EXPT. 181. *Synthesis of Para-rosaniline.*—Dissolve a gram of triphenylmethane in about 5 c.c. of cold fuming nitric acid, pour into water, filter, wash, dry on a porous plate, and dissolve in 5 c.c. of glacial acetic acid. Add gradually a gram of zinc dust from the point of a knife, and shake up. The colour changes to brown and the leuco-base of para-rosaniline is formed. It is diluted with water and precipitated with ammonia, and it is then filtered and dried. On gently warming the dry precipitate with a few drops of strong hydrochloric acid in a porcelain basin and adding a little water, a magenta coloration is produced, from the formation of para-rosaniline hydrochloride.

The series of reactions described in the above experiment, by which triphenylmethane is converted into para-rosaniline, is represented as follows—

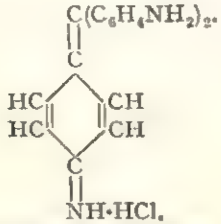
$$\underset{\text{Triphenylmethane.}}{HC\begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{cases}} \longrightarrow \underset{\text{Trinitrotriphenylmethane.}}{HC\begin{cases} C_6H_4NO_2 \\ C_6H_4NO_2 \\ C_6H_4NO_2 \end{cases}} \longrightarrow \underset{\text{Para-leucaniline.}}{HC\begin{cases} C_6H_4NH_2 \\ C_6H_4NH_2 \\ C_6H_4NH_2 \end{cases}}$$

$$\longrightarrow \underset{\text{Para-rosaniline base.}}{(HO)C\begin{cases} C_6H_4NH_2 \\ C_6H_4NH_2 \\ C_6H_4NH_2 \end{cases}}$$

By the action of hydrochloric acid on the base, the hydrochloride of para-rosaniline is formed, which is the soluble colouring matter—

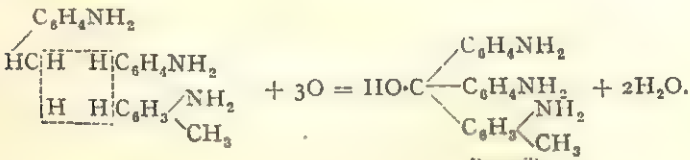
$$HO{\cdot}C(C_6H_4NH_2)_3 + HCl = C(C_6H_4NH_2)_3Cl + H_2O.$$

As in malachite green, the constitution of the hydrochloride is doubtful; but the quinonoid structure is generally accepted—



Para-rosaniline hydrochloride.

The formation of rosaniline from the mixture of aniline, *o*- and *p*-toluidine is represented by assuming that the methyl group of *p*-toluidine acts as the link which connects the nuclei of aniline and *o*-toluidine.



Rosaniline base.

Aniline Blue.—By replacing a hydrogen atom in each of the three amino-groups of rosaniline by phenyl groups, triphenylrosaniline, or aniline blue, is produced. The discovery was made by Girard and de Laire, and is effected by heating rosaniline base with aniline in presence of a small quantity of an organic acid, such as acetic or benzoic acid—

$$HO{\cdot}C(C_6H_4NH_2)_3 + 3C_6H_5NH_2 + 4C_2H_4O_2$$
$$= \underbrace{(C_2H_3O_2){\cdot}C(C_6H_4NH{\cdot}C_6H_5)_3}_{\text{Triphenylrosaniline acetate.}} + 3NH_4{\cdot}C_2H_3O_2 + H_2O.$$

Expt. 182.—Mix together in a boiling tube 1 gram of rosaniline base, 5 grams of aniline, and a few drops of glacial acetic acid, and heat for a quarter of an hour in a metal bath to 180°. Extract the colouring matter with methylated spirit. The solution is deep blue.

The salts of triphenylrosaniline are insoluble in water but soluble in alcohol. For this reason the hydrochloride of the base is some-

times known as *spirit blue*. It may be rendered soluble in water by sulphonation (p. 450), a fact discovered by Nicholson, and the soluble sulphonates are sometimes called *Nicholson's blues*. The sodium monosulphonate is usually termed *alkali blue*. It is used in a faintly alkaline solution for dyeing wool.

EXPT. 183.—Make a solution of alkali blue in water faintly alkaline with sodium carbonate, heat gently, and steep in it a skein of wool for a few minutes. Squeeze out the wool and introduce it into water acidified with hydrochloric acid. The blue colour is at once developed.

The colouring matter is absorbed by the fibre as the colourless sulphonate, and the blue is only developed after placing the wool in dilute acid. The sodium disulphonate dissolves in water with a deep blue colour, and is known as *cotton blue* or *water blue*.

EXPT. 184.—To dye cotton with cotton blue, the cotton must first be mordanted by steeping the cotton for a few hours previously in a 5 per cent. solution of tannin. The cotton is then squeezed out and placed in a similar solution of tartar emetic for an hour and washed thoroughly in hot water. The cotton is now impregnated with tannin, which, by forming an insoluble compound with tartar emetic, adheres to the fibre, and on bringing it into a warm and fairly concentrated solution of the blue it will take up the colour.

Methyl Violets.—The discovery of the aniline blues suggested the introduction of alkyl radicals into the amino-groups of rosaniline, and resulted in Hofmann's discovery of the methyl violets. He obtained the first of these dyes by heating rosaniline with methyl and ethyl iodide. The colours were known as *Hofmann's violets*, and were probably mixtures of tetra- and penta-methyl- and ethyl-rosanilines. He found in the mother-liquors from the violet a green colouring matter, which was separated and used under the name of *iodine green*. It is the quaternary methyl-ammonium iodide of the tetramethyl compound of rosaniline.

$$I{\cdot}C\begin{cases} C_6H_3(CH_3)N(CH_3)_2{\cdot}CH_3I. \\ C_6H_4{\cdot}NHCH_3 \\ C_6H_4{\cdot}NHCH_3 \end{cases}$$

Iodine green.

Neither the Hofmann violets nor iodine green are any longer employed for dyeing. They were soon replaced by similar colours, but prepared in a different and less expensive fashion, known as *methyl violet* and *methyl green*.

Methyl violet is obtained by oxidising dimethylaniline with cupric chloride. It is a mixture consisting mainly of tetra- and penta-methyl pararosaniline. It is probably formed by the oxidation of one of the methyl groups of dimethylaniline, which is removed as formaldehyde and serves as the link to the three dimethylaniline molecules.

$$\begin{array}{l} H\,C_6H_4N(CH_3)_2 \\ H\cdot CHO + H\,C_6H_4N(CH_3)_2 + O_2 = HO\cdot C \begin{cases} C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2 \\ C_6H_4NHCH_3 \end{cases} + 2H_2O. \\ H\,C_6H_4NHCH_3 \end{array}$$

Base of Pentamethyl para-rosaniline.

Expt. 185.—Place in a porcelain basin about 40 grams of common salt, mix it well with 0·3 gram of powdered cupric chloride, pour in about 1 c.c. of dimethylaniline and a few drops of glacial acetic acid, and mix. Warm the basin gently over a small flame with constant stirring. After a minute or two the violet colour of methyl violet appears, and in a short time the whole mass changes to a bronze-coloured powder. This is a double chloride of the colour base with cupric chloride, from which the colouring matter is separated by precipitating the copper with hydrogen sulphide. The violet colour of the substance is shown by mixing some of the product with water acidified with a little dilute hydrochloric acid to which sodium acetate solution is then added.

Methyl green is formed from methyl violet by acting upon the violet with methyl chloride. The compound has a similar composition to that of iodine green, the methyl chloride replacing the methyl iodide. Methyl green quickly loses the molecule of methyl chloride on heating, and is converted into the original violet compound.

Expt. 186.—Dye a strip of filter paper in methyl green, and warm it cautiously over a small flame. The colour soon changes to violet.

The formation of the green colour in the quaternary compounds is attributed to the formation of a quaternary ammonium group, which neutralises one of the basic groups, whereby the compound is practically converted into a derivative of malachite green.

Crystal Violet is the hexamethyl derivative of para-rosaniline. It was the first of the violets to be obtained in a pure and crystalline form. It is prepared by the action of dimethylaniline on tetramethyldiamino-benzophenone. The benzophenone derivative,

or *Michler's ketone,* is formed by the action of carbonyl chloride on dimethylaniline—

$$COCl_2 + 2C_6H_5N(CH_3)_2 = CO\begin{cases} C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2 \end{cases} + 2HCl.$$

Michler's Ketone.
(Tetramethyldiaminobenzophenone.)

When equivalent molecules of the ketone and dimethylaniline react in presence of an acid chloride (phosphorus tri- or oxychloride), the hydrochloride of hexamethyl pararosaniline is formed.

$$\begin{array}{c} CO[C_6H_4N(CH_3)_2]_2 \\ + \\ H|C_6H_4N(CH_3)_2 \end{array} = HO{\cdot}C[C_6H_4N(CH_3)_2]_3.$$

Base of crystal violet.

The base is converted into the hydrochloride by the phosphorus chloride.

Expt. 187.—Take about 0·25 gram each of Michler's compound and dimethylaniline, and add a few drops of phosphorus tri- or oxychloride. In a few moments the colour changes to a deep blue. Pour into a large volume of water containing sodium acetate. The colour now assumes a blue-violet tint.

Auramine, which is an important yellow dye, is also prepared from Michler's ketone by fusing it with ammonium chloride and zinc chloride—

$$OC\begin{cases} C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2 \end{cases} + NH_3 = HN{:}C\begin{cases} C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2 \end{cases} + H_2O.$$

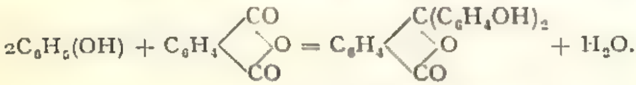
Auramine.

Expt. 188.—Take about 0·5 gram each of Michler's ketone, ammonium chloride, and powdered zinc chloride, and heat over a small flame until the mass fuses quietly. The deep orange-coloured product dissolves in alcohol or hot water with a yellow colour.

Phthaleins

The compounds which are known as *phthaleins* are obtained by heating phthalic anhydride with the phenols. The simplest of these compounds is phenolphthalein. The phthaleins form soluble salts with the alkalis, which possess a brilliant and frequently a fluorescent colour.

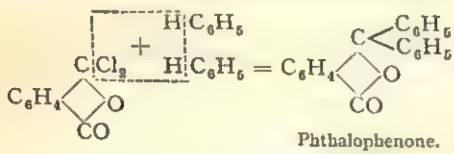
Phenolphthalein.—When two molecules of phenol and one molecule of phthalic anhydride are heated together to 115°, with the addition of strong sulphuric acid, phenolphthalein is formed—



Phenolphthalein.

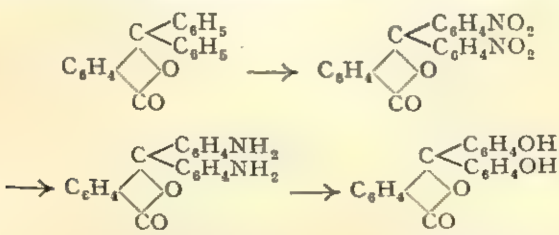
It is a white, crystalline substance which melts at 250°–253°; it is very slightly soluble in water, but dissolves readily in hot alcohol. It retains its character as a phenol, and dissolves in caustic alkalis with a crimson colour. It is used in alkalimetry and acidimetry as an indicator for the titration of weak (organic) acids with caustic alkalis and alkaline earths, but cannot be used with ammonia. It also gives a pink colour with the alkaline carbonates, but not the bicarbonates, and can be employed for determining the point of conversion of the neutral into the acid carbonate on the addition of acids.

The constitution of phenolphthalein has been determined by its synthesis from phthalyl chloride and benzene by means of the Friedel-Crafts reaction. Phthalyl chloride (p. 498) and benzene in presence of aluminium chloride form *phthalophenone*—



Phthalophenone.

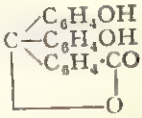
Phthalophenone is then converted successively into dinitro-, diamino-, and, finally, by the action of nitrous acid, into dihydroxyphthalophenone, or phenolphthalein—



Diamino-phthalophenone. Phenolphthalein.

The relation of phenolphthalein to triphenylmethane will be easily realised by a slight change in the manner of writing the formula (I.). The *quinonoid* structure is not so readily formulated. It has been represented by giving to the compound the form of an acid (II.).

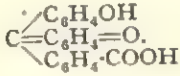
I.



Phenolphthalein.

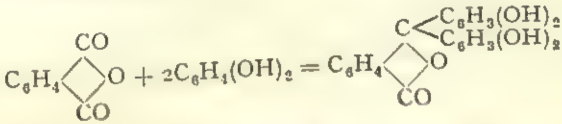
or

II.

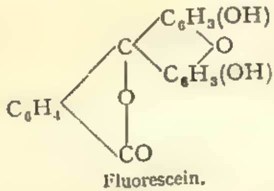


Phenolphthalein (Quinonoid formula).

Fluorescein.—A more important substance than phenolphthalein is fluorescein, which is used in the manufacture of the eosin dyes. Fluorescein is obtained as already explained (p. 467) by heating together to 200° (without the aid of sulphuric acid) phthalic anhydride and resorcinol. It is formed in the same manner as phenolphthalein.



At the same time, the tetrahydroxy-compound loses water and forms fluorescein—

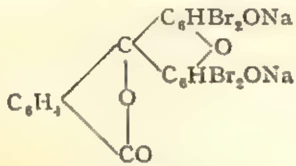


Fluorescein.

Fluorescein forms a red powder, which is insoluble in water, but dissolves in alcohol and dilute alkaline solutions with a brilliant green fluorescence. It is occasionally used as a dye for silk and wool, and imparts to the fibre a yellow, fluorescent effect.

Eosin.—By the action of the halogens on fluorescein, dissolved in acetic acid or alcohol, the eosins are obtained, colouring matters which are characterised, like fluorescein, by their fluorescence in

alkaline or alcoholic solution, but they possess a pink instead of a green colour. The formula for the sodium salt of tetrabromo-fluorescein, or ordinary eosin, is represented thus—

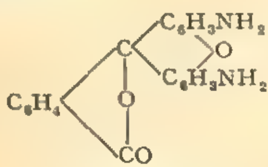


Eosin.

Erythrosin is the corresponding tetriodo-compound.

Expt. 189.—Dissolve about 0·25 gram of fluorescein in alcohol; cool, and add a little bromine water. If the solution is now made alkaline with caustic soda, a deep red-green fluorescent solution is obtained, which has a pink colour when diluted with water.

An important group of brilliant red dyes, known as the **rhodamines,** is obtained from phthalic anhydride and meta-amino-phenol and its derivatives. They have a constitution similar to that of fluorescein. The simplest of these compounds is represented by the following formula—



Rhodamine.

Aurin and Rosolic Acid.—Rosolic acid was originally obtained from coal-tar. It has been synthesised by oxidising a mixture of phenol and cresol with arsenic acid and sulphuric acid. Aurin is prepared by heating together phenol, oxalic and strong sulphuric acids. Rosolic acid and aurin dissolve in alkalis and alcohol with a bright red colour, but they are now little used as dyes. Their close connection with para-rosaniline has been shown in the following way. By heating aurin with ammonia under pressure, para-rosaniline is formed; by diazotising para-rosaniline and rosaniline and boiling the product with water, the amino-groups in both cases are replaced by hydroxyls, and aurin and rosolic acid are

produced. The formulæ of the two compounds are therefore represented as follows—

$$C\begin{cases} C_6H_4OH \\ C_6H_4OH \\ C_6H_4{=}O. \end{cases} \qquad\qquad C\begin{cases} C_6H_3(CH_3)OH \\ C_6H_4OH \\ C_6H_4{=}O. \end{cases}$$

Aurin. Rosolic acid.

Indigo is the blue colouring matter obtained from the leaves of the indigo-plant (*Indigofera sumatrana* and *arrecta*), which grows in India and Java. The blue colour from woad (*Isatis tinctoria*), a European plant, appears to be a distinct substance. The indigo is not present as such in the plant, but as indoxyl glucoside or *indican*, which undergoes hydrolysis during spontaneous fermentation, which sets in when the leaves are steeped in water—

$$\underset{\text{Indican or Indoxyl glucoside.}}{C_{14}H_{17}O_6N} + H_2O = \underset{\text{Indoxyl.}}{C_8H_7ON} + \underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

The indoxyl becomes oxidised by exposure to the air (see p. 529) and the indigo then separates as a blue, insoluble powder, which is washed and dried. It comes into the market in the form of irregular lumps, which, when rubbed against a hard surface, show a coppery lustre. The sugar with which the indigo is combined is dextroglucose.

Commercial indigo is not a pure substance, but contains varying quantities of other colouring matters (indirubin, indigo brown), as well as indigo gelatine, etc. Indigo is purified by crystallisation from aniline and other solvents or by sublimation. Pure indigo blue is known as *indigotin*.

Expt. 190.—Place a few grams of powdered indigo in a small porcelain basin, and, nearly in contact with it, a circular sheet of asbestos paper which is kept in position by a funnel placed on the top. The basin is heated to a high temperature on a sand-bath. In the course of about half an hour needle-shaped crystals with a brilliant coppery lustre will be found attached to the asbestos paper.

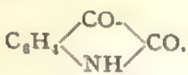
For dyeing wool the insoluble indigo is sulphonated and converted into the soluble disulphonic acid, or *indigocarmine*.

Expt. 191.—Add strong sulphuric acid to a little indigo, and warm gently. If the liquid is poured into water a clear blue solution is obtained, showing that the indigo, which is itself insoluble in water, has formed a soluble sulphonic acid. A small skein of wool, previously moistened, when left in the hot, dilute solution for a short time takes up the colouring matter and is dyed blue.

For dyeing cotton, indigo carmine is not employed, but an *indigo-vat* is prepared, in which the indigo is present in the dissolved state. The solubility of the indigo in this case depends upon the reduction of indigo to *indigo white*, a colourless substance which forms soluble salts with the caustic alkalis and alkaline earths. The reduction is usually effected with alkaline reducing agents, and the resulting solution is called an indigo-vat. The reducing agents commonly employed are ferrous sulphate and lime, or sodium hydrosulphite, $Na_2S_2O_4$. This solution rapidly oxidises on exposure to air, and indigo blue is precipitated. When the cotton is immersed in the liquid, it absorbs the indigo white which on removal from the liquid changes to blue and remains firmly attached to the fibre. Indigo blue is one of the fastest of the organic dyes, and resists the action of soap and light.

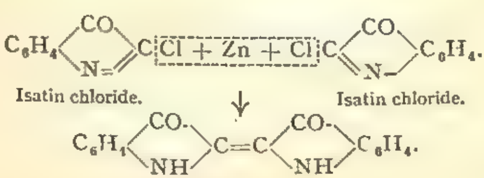
Expt. 192.—Heat a little finely powdered indigo with zinc dust and caustic soda solution or with a strong solution of sodium hydrosulphite. The indigo dissolves and gives a dark yellow solution, the yellow colour being due to impurities. Pour a little of the solution into water. As soon as the liquid falls into the water it instantly forms a blue precipitate. Place a skein of wet cotton in the remainder of the liquid, withdraw it and expose it for a few seconds to the air, and then wash it in water. The cotton is permanently dyed.

When indigo is oxidised with nitric acid it forms **isatin**. The structure of isatin is known from its synthesis, which need not be discussed—



Isatin.

Isatin chloride is obtained from isatin by the action of phosphorus chloride. The first synthesis of indigo was by the action of zinc dust and acetic acid on isatin chloride, and is formulated as follows :—



Indigo blue.

Two molecules of isatin chloride combine, chlorine being removed and hydrogen taken up by the two nitrogen atoms.

Another synthetic method is the action of grape-sugar and caustic soda solution on *o*-nitrophenylpropiolic acid (p. 504)—

$$2C_6H_4\left<\begin{matrix}C\vdots C\cdot COOH\\NO_2\end{matrix}\right. + 2H_2 = C_{16}H_{10}N_2O_2 + 2H_2O + 2CO_2.$$

EXPT. 193.—Dissolve a few grams of grape-sugar in a beaker of warm water, add a little *o*-nitrophenylpropiolic acid on the end of a glass rod, and then a little caustic soda solution. Provided the water is warm, the formation of indigo takes place rapidly.

A third synthesis is by using *o*-nitrobenzaldehyde (p. 477), acetone, and dilute caustic soda solution.

$$2C_6H_4\left<\begin{matrix}CHO\\NO_2\end{matrix}\right. + 2CH_3\cdot CO\cdot CH_3 = C_{16}H_{10}N_2O_2 + 2CH_3\cdot COOH + 2H_2O.$$

EXPT. 194.—Dissolve *o*-nitrobenzaldehyde in a little acetone, add 1 c.c. of a very dilute solution of caustic soda, and warm gently. Indigo blue is deposited.

One method of manufacture is from anthranilic acid (p. 490) and chloracetic acid. When heated they combine and form phenylglycine-*o*-carboxylic acid—

$$C_6H_4\left<\begin{matrix}COOH\\NH\vdots H + Cl\vdots CH_2\cdot COOH\end{matrix}\right. = \underset{\substack{\text{Phenylglycine-}\\ o\text{-carboxylic acid}}}{C_6H_4\left<\begin{matrix}COOH\\NH\cdot CH_2\cdot COOH\end{matrix}\right.} + HCl.$$

On fusion with potash, indigo is formed. The process takes place in two steps. In the first, a substance known as **indoxyl** is produced, which in the alkaline melt oxidises and forms indigo—

$$1.\quad C_6H_4\left<\begin{matrix}COOH\\NH\cdot CH_2\cdot COOH\end{matrix}\right. = \underset{\text{Indoxyl.}}{C_6H_4\left<\begin{matrix}CO\\NH\end{matrix}\right>CH_2} + CO_2 + H_2O.$$

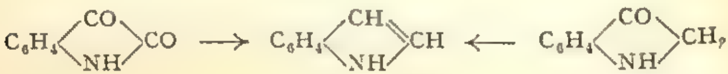
$$2.\quad 2C_6H_4\left<\begin{matrix}CO\\NH\end{matrix}\right>CH_2 + O_2 = \underset{\text{Indigo.}}{C_6H_4\left<\begin{matrix}CO\\NH\end{matrix}\right>C{=}C\left<\begin{matrix}CO\\NH\end{matrix}\right>C_6H_4} + 2H_2O.$$

EXPT. 195.—Mix in a hard glass test-tube 2 grams of phenylglycine *o*-carboxylic acid and 5 grams of coarsely powdered caustic potash and close the tube loosely with a cork. Heat for a minute or two until

the mass fuses and turns to a deep orange colour. On dissolving in water and exposing the liquid to the air, a precipitate of indigo blue is thrown down.

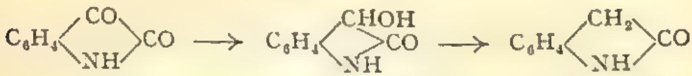
Another and simpler method is to heat phenyl glycine with sodamide, which forms, as above, indoxyl.

Isatin and indoxyl may be looked upon as derivatives of the parent substance **indole,** which is obtained by distilling isatin with zinc dust or indoxyl in alkaline solution.



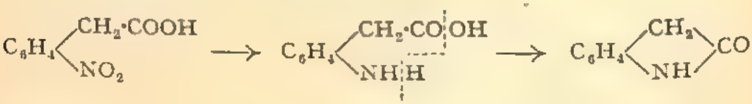
Isatin. Indole. Indoxyl.

When isatin is reduced with zinc dust and acetic acid it gives *dioxindol,* which can be further reduced by sodium amalgam to *oxindol,* an isomer of indoxyl. Like the latter, oxindol yields indole on distillation with zinc dust—



Isatin. Dioxindol. Oxindol.

The constitution of oxindol is indicated by its production from *o*-nitrophenyl acetic acid on reduction—



Questions on Chapter XXXVI

1. What is meant by *multinuclear hydrocarbons?* Give examples.
2. Describe the preparation of *diphenyl.* How would you propose to prepare benzidine from it? What is the customary process?
3. Give an example of the use of benzidine for the preparation of dyes.
4. Explain why *p*-nitrotoluene cannot be converted into tolidine. What is the structure of the tolidines that are known?
5. Describe the preparation of *diphenylmethane* and *triphenylmethane.* What products do they give on oxidation? Contrast this reaction with the behaviour of the paraffins.

6. Give the alternative formulæ for *malachite green*. Explain the relation of the colouring matter to the leuco-base and the base. How is the leuco-base obtained?

7. Describe the synthesis of *para-rosaniline*, and explain by means of it the formation of rosaniline. What is the nitrobenzene process for preparing rosaniline?

8. What is *aniline blue?* How is it prepared and in what form is it used as a dye?

9. Give a short account of the development of the methods for obtaining violet dyes. How do you explain the formation of *methyl violet* and *crystal violet?* How are these substances converted into green colouring matters and what explanation has been given of the change?

10. Discuss the structure of phenolphthalein. Explain its use as an indicator.

11. Give a general description of the manufacture of *eosin* from phthalic acid and resorcinol.

12. What is *aurin*, and what is its relation to para-rosaniline?

13. How does indigo occur in Nature, and how is it obtained from the natural source?

14. Describe those properties of indigo which render it available for dyeing wool and cotton.

15. What product does indigo yield on oxidation, and how can indigo be obtained from that product?

16. Describe any method by which indigo has been synthesised.

CHAPTER XXXVII

NAPHTHALENE AND ITS DERIVATIVES

Condensed Nuclei.—In previous chapters a variety of hydrocarbons and their derivatives have been described, some containing one, others more than one, benzene nucleus, linked together in different ways. Naphthalene affords an example of an aromatic hydrocarbon of a somewhat different type. According to present views, naphthalene contains two benzene nuclei which are not distinct, but have two carbon atoms in common. In anthracene (p. 550) and phenanthrene (p. 558) three nuclei are fused together, or condensed, in a similar way. They are examples of **condensed nuclei.**

Naphthalene, $C_{10}H_8$, is contained in the middle oil distillate of coal-tar (p. 386), from which, on standing, a portion frequently crystallises. A further quantity is obtained by fractionating the same oil after the phenol has been separated with caustic soda (p. 460). When the uncrystallisable oil, which first distils, is removed, the subsequent distillate solidifies. This is impure naphthalene. It is purified by treatment with a little strong sulphuric acid, which forms soluble sulphonic acids with the impurities, so that on washing with water they are dissolved out. The naphthalene is then sublimed or distilled in steam. It crystallises in plates, which melt at 79° and boil at 218°.

Naphthalene is extremely volatile, even far below its boiling-point, so that in the coal-gas manufacture a little of it passes through the scrubbers and purifiers and finds its way into the gas-pipes, where it occasionally accumulates in sufficient quantity to obstruct the flow of gas. It burns with a luminous, smoky flame, and is utilised for increasing the illuminating power of (*i.e.* carburetting) coal-gas. This is well illustrated in the *albo-carbon lamp,* where the coal-gas in its passage to the burner can be directed into a small metal chamber containing solid naphthalene, which is warmed by

the heat of the gas flame. A little naphthalene volatilises and mixes with the coal-gas, adding considerably to its luminosity.

Naphthalene acts as a vermin killer and as a mild antiseptic; but its chief industrial use is in the manufacture of phthalic anhydride, from which many important dyestuffs are obtained.

The formula of naphthalene is $C_{10}H_8$, and in its chemical properties it resembles benzene. It can be chlorinated, brominated, nitrated, and sulphonated in the same way, and gives very similar products. The following are the formulæ of some of these products—

$C_{10}H_7Cl$. Chloronaphthalene.	$C_{10}H_7NO_2$. Nitronaphthalene.	$C_{10}H_7{\cdot}SO_3H$. Naphthalene sulphonic acid.
$C_{10}H_6Cl_2$. Dichloronaphthalene.	$C_{10}H_6(NO_2)_2$. Dinitronaphthalene.	$C_{10}H_6(SO_3H)_2$. Naphthalene disulphonic acid.

Naphthalene forms amino-compounds (naphthylamines), which, like the amino-derivatives of benzene, can be diazotised. The sulphonic acids can be converted into phenols (naphthols) by fusion with caustic alkalis; or into cyanides (naphthyl cyanides) by distillation with potassium cyanide.

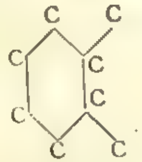
Naphthalene also forms additive products with hydrogen and chlorine. *Tetrahydronaphthalene*, $C_{10}H_{12}$ and *decahydronaphthalene*, $C_{10}H_{18}$, are obtained by the catalytic reduction of naphthalene by hydrogen under pressure in the presence of nickel. They are called *tetralin* and *decalin*, respectively, and are useful solvents and substitutes for turpentine. *Naphthalene dichloride* is prepared by adding hydrochloric acid to a mixture of naphthalene and potassium chlorate (prepared moist and dried); *naphthalene tetrachloride* is formed by passing chlorine into a chloroform solution of naphthalene. The first is a yellow liquid, the second a solid melting at 182°.

$C_{10}H_8Cl_2$. Naphthalene dichloride.	$C_{10}H_8Cl_4$. Naphthalene tetrachloride.

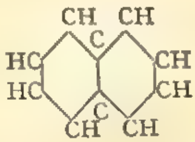
Structure of Naphthalene.—From the close analogy existing between naphthalene and benzene, one is naturally led to infer that naphthalene contains a benzene nucleus, and this view is

apparently confirmed by the behaviour of naphthalene on oxidation, for it readily yields phthalic acid (p. 497) when oxidised by air in the presence of vanadium pentoxide.

Phthalic acid contains a carbon skeleton of 8 atoms, 6 in the benzene ring and 2 in the ortho-position outside it—



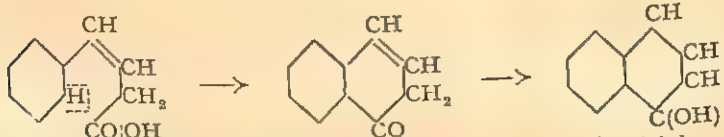
Now if the carbon atoms of naphthalene outside the benzene ring are joined so as to complete a second ring of 6 carbon atoms, and, if to each of the 8 outlying carbon atoms of the two rings a hydrogen atom is attached, such a structure would give the necessary number of carbon and hydrogen atoms required by the formula for naphthalene—



It would account, moreover, for the stability of the compound and its similarity to benzene. This structural formula represents two benzene rings, yet different from any previous combination, inasmuch as two carbon atoms are common to the two nuclei. It is commonly called a system of condensed nuclei.

Let us now examine the experimental evidence upon which this structure rests.

We may first refer to an interesting synthesis of α-naphthol (hydroxynaphthalene) discovered by Fittig by heating phenylisocrotonic acid (p. 503)—



Phenylisocrotonic acid. (Intermediate compound.) Naphthol.

Another synthesis has been effected by passing phenylbutylene, or phenylbutylene bromide, over red-hot soda-line—

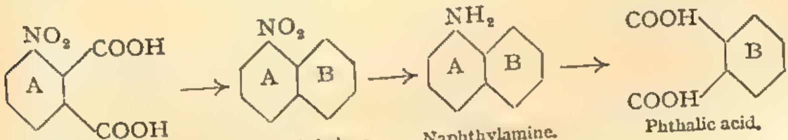
$$C_6H_5\begin{array}{l}\diagup CH_2-CH_2 \\ \qquad\quad\; | \\ \diagdown CH_2=CH\end{array} = C_6H_4\begin{array}{l}\diagup CH=CH \\ \qquad\quad\; | \\ \diagdown CH=CH\end{array} + 2H_2.$$

Phenylbutylene. Naphthalene.

Both syntheses, however, only point with certainty to the presence of one benzene ring in the compound.

More conclusive and complete is the experimental evidence of Graebe.

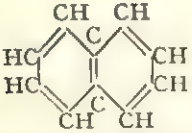
It has been stated that when naphthalene is oxidised, it forms phthalic acid, which is a benzene derivative. In the same way, if nitro-naphthalene is oxidised it yields nitro-phthalic acid. The benzene ring (A), with the nitro-group, remains intact. If, however, the nitro-compound is reduced, the product, naphthylamine (amino-naphthalene), gives phthalic acid on oxidation. In this case it is the ring (A) which has been destroyed; the second benzene ring (B) has been preserved. Two benzene rings are consequently present in naphthalene. The position in the ring of the nitro- or of the amino-group does not matter—



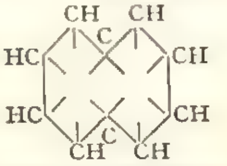
Nitrophthalic acid. Nitronaphthalene. Naphthylamine. Phthalic acid.

It follows that naphthalene is a combination of two benzene nuclei, that is of two 6-membered rings. Consequently the two carboxyl-groups of phthalic acid must be ortho- to one another, otherwise one of the rings of naphthalene would consist of more than six carbon atoms. Hence the xylene which gives rise to phthalic acid must be *o*-xylene (p. 395).

In naphthalene, as in benzene, we are met by the difficulty of disposing of the fourth carbon bond. The formula with alternate double bonds, proposed by Kekulé for benzene, was applied by Erlenmeyer to naphthalene, and seems a natural and logical consequence of the relation of the two hydrocarbons—



Erlenmeyer's formula for Naphthalene.



Bamberger's centric formula.

But a similar set of objections to those advanced against the olefinic (Kekulé) formula for benzene may be brought against Erlenmeyer's formula for naphthalene.

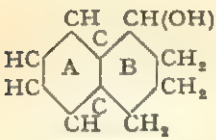
A modification of the centric formula was therefore advocated by Bamberger, but whereas the centric formula might possibly be applicable to the symmetrical structure of benzene, the problem of naphthalene is very different, since the bond which is common to both nuclei is now disrupted. An early attempt to rectify this defect was made by condensing one centric nucleus with one of the Kekulé type, thus—

It will be seen that the latter is not a benzenoid ring, since it contains only two double links, and should therefore be definitely olefinic in character like benzene dihydride, *cyclohexadiene*, C_6H_8. Experiment shows that naphthalene is in fact more unsaturated in character than benzene, and the presence of two double bonds is confirmed by the addition of hydrogen to form first the 1 : 4-dihydride and then the 1 : 2 : 3 : 4-tetrahydride, one ring being completely reduced before the other is attacked; also the fact that naphthalene combines with only two molecules of ozone affords additional proof of the presence of two double bonds. But Erlenmeyer's formula can be used equally well to account for this behaviour, for an oscillation of bonds, similar to that adopted for benzene, leads to the production of three phases, in two of which one ring contains only two double bonds—

Moreover, a study of the substitution products of naphthalene shows that there is no evidence of any difference in the constitution of the two nuclei, such as results from the modified centric formula. They seem to

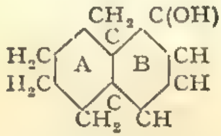
have the same properties. No difference has been detected between the α- and β-positions (p. 538) of one ring and corresponding positions of the other ring until substitution has actually taken place. As might be expected, the condensation of two aromatic nuclei to form naphthalene is accompanied by some slight modification in chemical reactivity. The greater degree of unsaturation of naphthalene has already been mentioned. The replacement of the hydroxyl group of the naphthols by the amino-group by the action of ammonia occurs more easily and at a much lower temperature than in the case of phenol, and the naphthols unlike the phenols, react readily with alcohols in the presence of hydrogen chloride to form ethers. Now, the naphthols can be reduced by sodium in amyl alcohol to give tetrahydrides, which more closely resemble phenols, but at the same time other products are formed which have completely lost their phenolic character and are in fact aromatic alcohols (similar to benzyl alcohol). Thus α-naphthol gives the two compounds represented by the formulæ—

I.



ac-Tetrahydronaphthol.

II.



ar-Tetrahydronaphthol.

In structure I the nucleus marked A retains its aromatic character, while that marked B has become aliphatic, though still cyclic, and is therefore said to be *alicyclic* (*ac.*). *Ac*-tetrahydronaphthol is a secondary alcohol. In the second structure reduction has taken place in ring A, which becomes aliphatic, while B remains aromatic, and in fact the compound *ar*-tetrahydronaphthol has reverted more closely to the character of phenol. The two naphthols and the two naphthylamines behave similarly in this respect, each yielding 2 tetrahydrides, the α-compounds giving *ar*-derivatives and the β-compounds *ac*-derivatives as the chief products. Thus it appears that each of the two nuclei can revert to the benzenoid type by reduction of the other. We may infer therefore that a hybrid structure like that of the modified centric formula is not justified. The centric formula for naphthalene has therefore been abandoned; nor is it favoured for benzene itself, since it conflicts with the planar configuration of the 12 atoms of benzene, that has been deduced from X-ray analysis. Hence formulæ of the Kekulé type have not been superseded, since they are superior to all the others hitherto devised, and can be used to illustrate the chemical

The β-*chloronaphthalene* cannot be prepared by direct chlorination but is obtained from β-naphthylamine (p. 434) by means of the diazo-reaction—

$$1.\ \underset{\beta\text{-Naphthylamine.}}{C_{10}H_7NH_2} \longrightarrow \underset{\beta\text{-Naphthalene diazonium chloride.}}{C_{10}H_7N_2Cl} \longrightarrow \underset{\beta\text{-Chloronaphthalene.}}{C_{10}H_7Cl.}$$

or by the action of phosphorus chloride on β-naphthol—

$$2.\ \underset{\beta\text{-Naphthol.}}{C_{10}H_7OH} + PCl_5 = \underset{\beta\text{-Chloronaphthalene.}}{C_{10}H_7Cl} + POCl_3 + HCl.$$

β-Chloronaphthalene is a solid which melts at 56° and boils at 265°. All the ten dichloronaphthalenes are known.

The halogen atoms as well as the nitro-, sulphonic, and hydroxyl groups are less firmly fixed in the molecule of naphthalene than in that of benzene, and undergo changes more readily. An example of this, among others to be presently mentioned, is the conversion of α-nitronaphthalene into α-chloronaphthalene by the action of phosphorus pentachloride.

Nitro-derivatives of Naphthalene.—Only α-nitronaphthalene, m.p. 61°, is obtained by direct nitration of naphthol with strong nitric acid.

The second nitro-groups likewise enter the α-positions (8 and 5). β-Nitronaphthalene consequently cannot be prepared by any direct method. It is obtained from β-naphthylamine by a curious application of the diazo-reaction. The β-naphthylamine is converted into naphthalene diazonium nitrite by adding sodium nitrite to the nitrate of the base. Finely divided cuprous oxide is then added, when effervescence occurs from the evolution of nitrogen, and β-nitronaphthalene is formed. It melts at 79°.

$$\underset{\beta\text{-Diazonaphthalene nitrite.}}{C_{10}H_7 \vdots N_2 \vdots ONO} = \underset{\beta\text{-Nitronaphthalene.}}{C_{10}H_7NO_2} + N_2.$$

Naphthylamines.—The two α- and β-naphthylamines resemble aniline, and are prepared by similar methods.

α-*Naphthylamine* is obtained by the reduction of α-nitronaphthalene, or by heating α-naphthol with the compound of ammonia with zinc chloride, or calcium chloride, to 250°.

$$C_{10}H_7OH + NH_3 = C_{10}H_7NH_2 + H_2O.$$

The latter reaction has been applied to ordinary phenol (p. 459), but, in the case of the naphthols, the change is much more easily accomplished (see below), and is another instance of the mobility of the groups in naphthalene derivatives.

α-Naphthylamine crystallises in colourless needles which melt at 50° and boil at 300°.

Expt. 196.—*Reactions for α-Naphthylamine.*—1. Add to a few grams of α-naphthylamine a solution of dilute hydrochloric acid insufficient to dissolve the base on shaking. Pour off the solution and add $FeCl_3$. A blue coloration of the liquid slowly develops. 2. Dissolve a very small quantity of the base in dilute alcohol, add a little glacial acetic acid, and then drop by drop sodium nitrite solution. A yellow solution is obtained, which on the addition of dilute hydrochloric acid changes to violet.

β-*Naphthylamine* is not prepared from nitronaphthalene, as the preparation of the base involves that of the nitro-compound (p. 540); but the action of ammonia under pressure on β-naphthol can be applied and is commercially used as the source of this compound. β-Naphthylamine melts at 112° and boils at 294°.

Sulphonic Acids of Naphthalene.—When naphthalene is heated with strong sulphuric acid, both the α- and β-naphthalene monosulphonic acids, $C_{10}H_7{\cdot}SO_3H$, are formed, which vary in relative quantity according to the temperature of the reaction. The α-compound predominates at a low temperature (80°); the β-compound at the higher temperature (160°).

The sulphonic acids resemble in properties the corresponding derivatives of benzene. They are very soluble and form soluble salts. By fusion with potash they form naphthols, and by distillation with potassium cyanide yield cyanides. Phosphorus pentachloride converts them into sulphonic chlorides, which have the properties of the corresponding benzene compounds (p. 452). Di- and tri-sulphonic acids of naphthalene are obtained by using fuming sulphuric acid containing different quantities of sulphur trioxide.

Naphthylamine sulphonic acids are important industrial products being largely applied in the manufacture of azo-dyes. Among these may be mentioned **naphthionic acid**, or 1-4-naphthylamine sulphonic acid, $C_{10}H_6(NH_2)SO_3H$, which is obtained by heating

α-naphthylamine sulphate in vacuo to 130°. It is the analogue of sulphanilic acid (p. 424) among the naphthalene compounds, and is used in the production of Congo-red and the benzopurpurin colours (p. 445).

EXPT. 197.—To show the similarity in properties of sulphanilic acid and naphthionic acid, take about 0·5 gram of each acid in separate test-tubes, add a few drops of sodium nitrite solution and a few c.c. of dilute hydrochloric acid, and pour a little of each solution into test glasses containing about 1 gram of β-naphthol dissolved in caustic soda and diluted with water. Bright red azo-colours of different shades will be produced.

β-Naphthylamine gives, according to the temperature of the reaction, one or other of four isomeric sulphonic acids. Many of the disulphonic acids are also commercial products.

Naphthols are the naphthalene representatives of the phenols, and share their general characters, although they exhibit some minor differences in chemical behaviour. The hydroxyl group is more readily replaced by ammonia, as we have seen in the formation of the naphthylamines (p. 540), and the ethers are prepared by the combined action of alcohol and sulphuric acid after the fashion of ethyl ether. A number of the α- and β-naphthol monosulphonic acids, as well as disulphonic acids, are used in the manufacture of azo-dyes.

α-Naphthol, $C_{10}H_7(OH)$, is obtained by fusing naphthalene monosulphonic acid with caustic soda (p. 451), or from α-naphthylamine by means of the diazo-reaction (p. 433). Its synthesis from phenylisocrotonic acid has already been described (p. 534). α-Naphthol is sparingly soluble in water. It has a phenolic smell and is volatile. Ferric chloride gives a violet precipitate of dinaphthol, which is an oxidation product, and has the following structure—

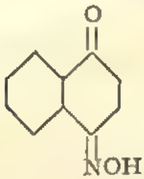
$$OH{\cdot}C_{10}H_6{\cdot}C_{10}H_6OH.$$

Dinaphthol.

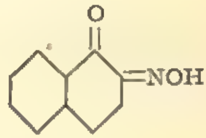
EXPT. 198. 1. *Reactions for α-Naphthol.*—Dissolve a little α-naphthol in very dilute alcohol and to the hot solution add $FeCl_3$. A flocculent violet precipitate of dinaphthol is thrown down. 2. To another portion of the same solution, when cold, add a solution of sodium hypochlorite. A green coloration is produced, changing, on further addition of the hypochlorite, to blue. 3. A cold saturated solution of

α-naphthol and of picric acid, when mixed, forms orange crystals of a picric acid compound. It should be remembered that α-naphthol is used as a reagent for carbohydrates (p. 292).

Naphthol forms with nitrous acid an α- and β-nitroso-α-naphthol, or naphthaquinonoxime (p. 482)—



α-Nitroso-α-naphthol.

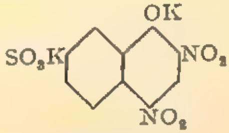


β-Nitroso-α-naphthol.

α-Naphthol melts at 94° and boils at 280°. By the action of nitric acid it is converted into nitro-derivatives, which correspond in chemical properties and colour to picric acid (p. 463), and like picric acid are used as dyes for silk and wool.

Martius' yellow, $C_{10}H_5(NO_2)_2ONa + H_2O$, is the sodium salt of dinitro-α-naphthol, and is obtained by the action of strong nitric acid upon α-naphthol.

Naphthol yellow is the potassium salt of dinitro-α-naphthol-sulphonic acid, and is prepared by the action of nitric acid on α-naphthol-trisulphonic acid—

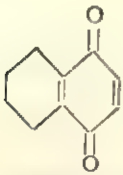


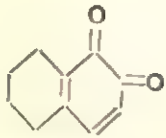
Naphthol yellow.

β-*Naphthol*, $C_{10}H_7(OH)$, is prepared from β-naphthalene sulphonic acid by fusion with caustic soda, which is the commercial process, or by the action of nitrous acid on β-naphthylamine. It crystallises in leaflets; it melts at 122° and boils at 286°. β-Naphthol is coloured green by ferric chloride, and also yields a precipitate of β-dinaphthol of a similar constitution to the α-compound. β-Naphthol and especially the sulphonic acid derivatives have an extensive application in the production of azo-dyes.

Naphthaquinones.—α-*Naphthaquinone*, $C_{10}H_6O_2$, corresponds

exactly to benzoquinone, both in its properties and method of preparation.

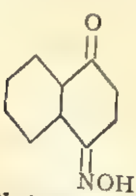

α-Naphthaquinone.

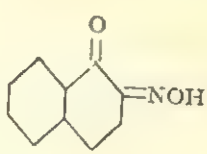

β-Naphthaquinone.


Amphi-naphthaquinone.

It is obtained by oxidising α-naphthylamine, 1-4-diamino- or dihydroxy-naphthalene, or 1-4-aminonaphthol, and also, though less readily, by the oxidation of naphthalene itself with chromic acid in acetic acid solution. It crystallises in yellow plates which sublime at 100° and are volatile in steam. It possesses, moreover, an unmistakable quinone smell. Sulphurous acid reduces it to 1-4-dihydroxynaphthalene.

β-*Naphthaquinone*, $C_{10}H_6O_2$, corresponds to ortho-quinone among the benzene derivatives. It is obtained by oxidising β-amino-α-naphthol with ferric chloride. Like ortho-quinone it crystallises in red needles, is without smell, and is non-volatile. It also resembles phenanthraquinone (p. 559). It is termed an *ortho-quinone*, or ortho-diketone, to distinguish it from the ordinary, or *para-quinone*. By the action of hydroxylamine each of the quinones yields a quinonoxime, or nitrosonaphthol, which are identical with the compounds obtained by the action of nitrous acid on α-naphthol (p. 543).


α-Naphthaquinonoxime, or
α-Nitroso-α-naphthol.


β-Naphthaquinonoxime, or
β-Nitroso-α-naphthol.

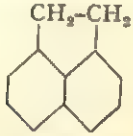
2 : 6- or *amphi-naphthaquinone* is prepared by oxidising 2 : 6-dihydroxynaphthalene. It is non-volatile and resembles the o-quinones.

Naphthoic Acids.—Naphthalene forms a series of carboxylic or naphthoic acids, which, however, afford fewer points of interest than the corresponding benzene derivatives, for they rarely occur in the products of plant life, nor have they as yet found any practical application.

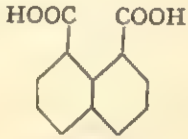
α-Naphthoic acid, $C_{10}H_7{\cdot}COOH$, is obtained by hydrolysis of the cyanide, $C_{10}H_7{\cdot}CN$, and by the action of chloroformamide on naphthalene in presence of aluminium chloride, precisely as in the synthesis of benzoic acid from benzene (p. 487). It melts at 160°.

β-Naphthoic acid is prepared from the β-cyanide and by the oxidation of the β-alkylnaphthalenes. It melts at 182°. Both acids resemble benzoic acid and give naphthalene when distilled with soda-lime.

Acenaphthene, $C_{12}H_{10}$, is a curious derivative of naphthalene which is found in coal-tar. It yields on oxidation a naphthalene dicarboxylic acid known as *naphthalic acid*, which contains the two carboxyl groups in the peri-positions. From the fact that this acid gives an anhydride on heating, and that acenaphthene is obtained by passing α-ethylnaphthalene through a red-hot tube, its structure has been interpreted as follows—



Acenaphthene.



Naphthalic acid.

Questions on Chapter XXXVII

1. How are the separation and purification of naphthalene from coal-tar effected? Describe the manufacture of phthalic acid from naphthalene.

2. Compare naphthalene and benzene. Discuss the experimental evidence upon which the double-hexagon formula for naphthalene rests.

3. Point out the relative merits of the naphthalene formulæ of Erlenmeyer and Bamberger.

4. Give the number of mono- and di-derivatives of naphthalene, What is the system of nomenclature adopted to distinguish the isomers? Denote by figures the relative positions of the chlorine atoms in the ten dichloronaphthalenes. Which of them is called the peri-position? What relation does it bear to the ortho-, meta-, or para-position?

5. Describe the preparation of α- and β-chloronaphthalenes, nitronaphthalenes, naphthylamines, and naphthols. Compare and contrast the properties of the isomers with the corresponding derivatives of benzene.

6. How are the naphtha-quinones obtained? Why are they regarded as ketones? What is meant by the terms ortho- and para-quinone? In what respects do they resemble or differ from the benzoquinones?

7. What is acenaphthene, and what is its relation to naphthalic acid and naphthalene?

8. Explain why it is assumed that the molecule of naphthalene is formed by the combination of two benzene residues in such manner that these have two carbon atoms in common.

9. Give the constitutional formulæ of the theoretically possible mono- and di-chloronaphthalenes. Describe a synthesis of α-naphthol which proves the constitution of this compound.

CHAPTER XXXVIII

ANTHRACENE AND ITS DERIVATIVES

Anthracene, $C_{14}H_{10}$ (ἄνθραξ, coal), occurs with its isomer phenanthrene and a variety of other compounds in the last portion of the distillate from coal-tar, known as anthracene oil (p. 386). The dark-coloured liquid deposits on standing a light brown, crystalline mass consisting of anthracene mixed with *phenanthrene* (p. 558) and *carbazole* (p. 577). It is filtered in a filter press, and washed with solvent naphtha free from adhering oil. The crystalline, pepper-coloured mass contains about 50 per cent. of anthracene, and is known commercially as 50 *per cent. anthracene*. This forms the raw material which is used on an extensive scale in the manufacture of alizarin and allied colouring matters (p. 554). The crude anthracene may be purified by distillation with the addition of a little solid caustic potash, which combines with the carbazole, forming potassium carbazole. The phenanthrene is removed with carbon bisulphide, in which it is much more soluble than anthracene.

Pure anthracene crystallises from benzene and other solvents in colourless plates with a lustrous surface and blue fluorescence. It melts at 213° and boils at 351°, and forms a compound with picric acid which crystallises in red needles.

EXPT. 199.—Dissolve picric acid and anthracene in about equal molecular proportions in glacial acetic acid, and pour them together. Red crystals soon deposit, and melt at 138°.

The majority of oxidising agents convert anthracene into anthraquinone.

$$\underset{\text{Anthracene.}}{C_{14}H_{10}} + 3O = \underset{\text{Anthraquinone.}}{C_{14}H_8O_2} + H_2O.$$

EXPT. 200.—*Estimation of Anthracene.*—The last reaction affords a simple means of estimating anthracene quantitatively. Dissolve one gram of crude anthracene in 45 c.c. of glacial acetic acid, and whilst

boiling with a reflux condenser attached to the flask, add 15 grams of chromic acid (CrO_3) dissolved in 10 c.c. of glacial acetic acid, diluted with an equal volume of water. Boil for an hour; then pour and rinse the contents into water. Filter, wash with a little dilute caustic soda and then with water, and dry. Dissolve the crude anthraquinone in strong, or slightly fuming, sulphuric acid at 100°, and expose the surface to a jet of steam until crystals begin to form: then pour into water, filter, wash, dry, and weigh. Sublime the anthraquinone by heating it in a basin, and estimate the loss of weight, which is that of pure anthraquinone. The anthracene is calculated from the amount of anthraquinone.

Properties of Anthracene.—Anthracene exhibits certain points of resemblance to benzene, and more particularly to naphthalene. It is converted by sulphuric acid into mono- and di-sulphonic acids. By the action of sodium amalgam in alcoholic solution, it forms *anthracene hydride*, $C_{14}H_{12}$, which readily passes back into anthracene on oxidation.

With chlorine both addition and substitution products are formed. The addition compound, *anthracene dichloride*, $C_{14}H_{10}Cl_2$, is obtained by passing chlorine into a cold solution of anthracene in carbon bisulphide, whilst the substitution product, *monochloranthracene*, $C_{14}H_9Cl$, is prepared by the action of potash on the dichloride—

$$C_{14}H_{10}Cl_2 + KOH = \underset{\text{Mono-chloranthracene.}}{C_{14}H_9Cl} + KCl + H_2O.$$

Dichloranthracene, $C_{14}H_8Cl_2$, is produced from anthracene by the action of chlorine at 100°. Both the mono- and di-chloranthracenes are yellow, crystalline compounds, which melt at 103° and 209° respectively, and give anthraquinone on oxidation.

It has already been stated that anthracene is readily oxidised to anthraquinone. The action resembles the oxidation of naphthalene to naphthaquinone, but in the case of anthracene the process is much more easily accomplished. The resemblance between the substances themselves is only apparent, for we shall see presently that anthraquinone has few of the properties of a true quinone.

Anthracene yields no nitro-derivatives when nitrated in the ordinary way, but is oxidised to anthraquinone. Anthraquinone is a remarkably stable substance and resists the action of the

ordinary oxidising agents; but some of its derivatives yield phthalic acid, and anthraquinone itself is converted into benzoic acid by the action of fused potash.

In reviewing the above reactions, it must be admitted that they afford little knowledge of the structure of anthracene. Much more valuable is the information derived from the synthesis of anthracene, anthracene hydride, and anthraquinone, which will now be described.

Synthesis of Anthracene.—Anthracene is obtained by the action of benzene on acetylene bromide (p. 392) in presence of aluminium chloride—

$$C_6H_6 + C_2H_2Br_4 + C_6H_6 = \underset{\text{Anthracene.}}{C_6H_4{\cdot}C_2H_2{\cdot}C_6H_4} + 4HBr.$$

It is also obtained by heating *o*-tolylphenylketone with zinc dust—

$$\underset{o\text{-Tolylphenylketone.}}{C_6H_4\left<\begin{array}{c}CH_3\\ \\ CO\end{array}\right>C_6H_5} = \underset{\text{Anthracene.}}{C_6H_4\left<\begin{array}{c}CH\\ |\\ CH\end{array}\right>C_6H_4} + H_2O.$$

Synthesis of Anthracene Hydride.—Anthracene hydride is formed together with anthracene and toluene by the action of aluminium chloride on benzyl chloride—

$$\underset{\text{Benzyl chloride.}}{C_6H_5\left/\begin{array}{c}CH_2Cl\\ +\\ CH_2Cl\end{array}\right/C_6H_5} = \underset{\text{Anthracene hydride.}}{C_6H_4\left<\begin{array}{c}CH_2\\ \\ CH_2\end{array}\right>C_6H_4} + 2HCl.$$

$$C_6H_4\left<\begin{array}{c}CH_2\\ \\ CH_2\end{array}\right>C_6H_4 + C_6H_5CH_2Cl$$
$$= \underset{\text{Anthracene.}}{C_6H_4\left<\begin{array}{c}CH\\ |\\ CH\end{array}\right>C_6H_4} + \underset{\text{Toluene.}}{C_6H_5CH_3} + HCl.$$

A second and very important synthesis is effected by boiling *o*-bromobenzyl bromide with sodium, for it indicates that the two central carbon atoms of the molecule of anthracene are linked

to both benzene nuclei in the ortho-positions, though it remains uncertain in which of two ways the combination occurs—

$$C_6H_4\left\langle\begin{matrix}CH_2 & Br\\ & Br\end{matrix}\right. + 4Na + \left.\begin{matrix}Br & \\ Br & CH_2\end{matrix}\right\rangle C_6H_4 = C_6H_4\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle C_6H_4 + 4NaBr.$$

o-Bromobenzyl bromide.

or—

$$C_6H_4\left\langle\begin{matrix}CH_2 & Br\\ & Br\end{matrix}\right. + 4Na + \left.\begin{matrix}Br & CH_2\\ Br & \end{matrix}\right\rangle C_6H_4 = C_6H_4\left\langle\begin{matrix}CH_2\cdot CH_2\\ \rule{3em}{0.4pt}\end{matrix}\right\rangle C_6H_4 + 4NaBr.$$

The second formula is excluded by the fact that anthracene is obtained from *o*-tolylphenylketone (see above). The second reaction does nevertheless occur at the same time, and gives rise to phenanthrene, described on p. 558.

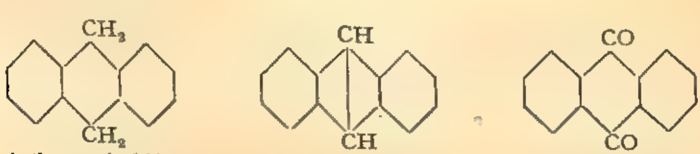
Synthesis of Anthraquinone.—Anthraquinone is manufactured by heating *o*-benzoylbenzoic acid with concentrated sulphuric acid at 150° C.

$$C_6H_4\left\langle\begin{matrix}CO\text{———}\\COOH\end{matrix}\right\rangle C_6H_5 = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4 + H_2O.$$

o-Benzoylbenzoic acid. Anthraquinone.

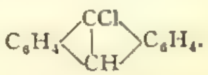
The various syntheses just described point unmistakably to the existence in anthracene and its derivatives of a framework of two benzene nuclei, joined together by two central carbon atoms, which are attached to adjacent or ortho-carbon atoms of the nuclei.

Seeing that anthracene is converted by reduction into anthracene hydride, and that anthracene is changed by oxidation into anthraquinone, the relation of the three is very simply expressed by the following formulæ—

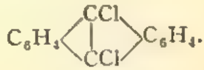


Anthracene hydride. Anthracene. Anthraquinone.

Moreover, as mono- and di-chloranthracene both yield anthraquinone on oxidation, the chlorine atoms, which disappear from the compound, must be attached to the central carbon atoms—



Monochloranthracene.

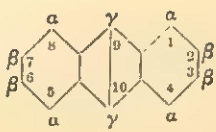


Dichloranthracene.

An alternative formula for anthracene is—

No completely satisfactory formula has yet been found. A noteworthy feature is the readiness with which anthracene is attacked by reagents in the central nucleus.

Isomerism of Anthracene Derivatives.—We are now in a position to compute the number of possible isomers which the derivatives of anthracene can give, and to adopt a system for distinguishing them. This system consists in numbering or lettering the carbon atoms as follows—



As in naphthalene, the eight outlying carbon atoms form two series of symmetrical positions of four each, which are distinguished as α- and β-positions, or numbered 1, 2, 3, 4, 5, 6, 7 and 8, as in naphthalene. There are, in addition, two central carbon atoms representing a third symmetrical series, which are distinguished as γ or 9 and 10 positions. There are consequently three mono-derivatives of anthracene, viz. α, β, and γ, and fifteen di-derivatives. Few of the second series are complete.

Anthraquinone, $C_{14}H_8O_2$, is one of the most important of the derivatives of anthracene, as it is the parent substance of a number of vat dyestuffs. Anthraquinone is manufactured by the oxidation of anthracene and also by synthesis from phthalic acid. Since phthalic acid can now be obtained economically by the atmospheric oxidation of naphthalene, which is considerably more abundant in coal-tar than anthracene, the synthetic method is likely to supersede the other. Moreover, it yields a much purer product. Oxidation of anthracene is effected with sodium dichromate and sulphuric acid, and the product is digested with concentrated sulphuric acid at 100° C. in order to convert the impurities into soluble sulphonic acids, which can be washed out. The anthraquinone is not attacked by the sulphuric acid. When dry it can be further purified by sublimation. Phthalic anhydride reacts with benzene in the presence of *excess* of anhydrous aluminium chloride to give *o*-benzoyl benzoic acid—

$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + C_6H_6 = C_6H_4\left\langle\begin{matrix}CO—C_6H_5\\COOH\end{matrix}\right.$$

from which anthraquinone is obtained (p. 550). This method has been adapted to the production of derivatives of anthraquinone by condensing the phthalic acid with substituted benzenes.

Anthraquinone crystallises in yellow needles, which melt at 277° C. and sublime at 250° C.; it is insoluble in water, but dissolves in glacial acetic acid and other organic solvents.

Structure of Anthraquinone.—From the synthesis described it follows that the central pair of carbon atoms is linked to at least one nucleus in the ortho-position. By a similar series of reactions bromophthalic anhydride can be converted into bromanthraquinone.

In this case the central pair of carbon atoms is attached to the substituted nucleus in the ortho-position.

Now, bromanthraquinone, when fused with potash, gives hydroxyanthraquinone, which on oxidation yields phthalic acid, the substituted nucleus being destroyed.

Consequently, the central carbon atoms are also linked to the unsubstituted nucleus in the ortho-position—

$$\boxed{(HO)C_6H_3}\left<\begin{matrix}CO\\ CO\end{matrix}\right>C_6H_4 \longrightarrow \left.\begin{matrix}HOCO\\ HOCO\end{matrix}\right>C_6H_4,$$

Hydroxyanthraquinone. Phthalic acid.

Anthraquinone exhibits the properties of a ketone in its behaviour with hydroxylamine, with which it forms an oxime. Moreover, on reduction with zinc dust and caustic soda, it yields a secondary alcohol, *oxanthranol*, which forms a red sodium compound, thus affording a delicate test for the detection of anthraquinone—

$$C_6H_4\left<\begin{matrix}CO\\ CO\end{matrix}\right>C_6H_4 + NaOH + Zn = C_6H_4\left<\begin{matrix}CO\text{———}\\ CH(ONa)\end{matrix}\right>C_6H_4 + ZnO.$$

Sodium oxanthranolate.

EXPT. 201.—Add a little caustic soda to a small quantity of anthraquinone, and then a little zinc dust. On heating to boiling, an intense red coloration is produced, which disappears on shaking. This arises from the sodium oxanthranolate becoming oxidised to anthraquinone on exposure to air.

With tin and hydrochloric acid, *anthranol* is formed; it is a substance possessing weak phenolic properties—

$$C_6H_4\left<\begin{matrix}CO\\ CO\end{matrix}\right>C_6H_4 + 2H_2 = C_6H_4\left<\begin{matrix}C(OH)\\ |\\ CH\text{——}\end{matrix}\right>C_6H_4 + H_2O.$$

Anthranol.

With a more vigorous reducing agent, as, for example, distilling with zinc dust, anthracene is formed. Compounds with the hydroxyl group in the α and β positions are more strongly phenolic than anthranol and are called α- and β-*anthrols*.

Anthraquinone possesses few of the characteristics of benzoquinone or naphthaquinone. It has no smell, nor does it sublime readily. Moreover, it cannot be reduced with sulphurous acid, although stronger reducing agents act upon it in the manner already explained.

Alizarin, *Dihydroxyanthraquinone*, $C_{14}H_6O_2(OH)_2$, is the principal colouring matter of madder (*Rubia tinctoria*). Madder root has been used as a dyestuff in India and Egypt from the earliest times,

and the process of dyeing cotton with a mordant is mentioned by Pliny. Madder owes its properties as a dye to alizarin and purpurin, which are present in the root as glucosides. The glucoside of alizarin is known as *ruberythric acid*, which is hydrolysed by acids or ferments, and breaks up into glucose and alizarin—

$$\underset{\text{Ruberythric acid.}}{C_{26}H_{28}O_{14}} + 2H_2O = \underset{\text{Glucose.}}{2C_6H_{12}O_6} + \underset{\text{Alizarin.}}{C_{14}H_8O_4}.$$

Madder root and the various extracts, which until fifty years ago were extensively employed in the production of *Turkey red* cloth and other dyed and printed fabrics, has been entirely superseded by artificial alizarin, purpurin, and similar colouring matters. The first important step in the synthesis of alizarin was made by Graebe and Liebermann in 1868, who found that when alizarin is heated with zinc dust it is reduced to anthracene.

Anthracene, well known as a constituent of coal-tar, was recognised for the first time as the parent substance of alizarin. Now, alizarin contains two atoms of oxygen more than anthraquinone, which, from the solubility of alizarin in caustic soda, are probably present as hydroxyl groups. In order to introduce two hydroxyl groups into anthraquinone, Graebe and Liebermann converted it into dibromanthraquinone by bromination, and then fused the product with potash. They were fortunate in obtaining the one dihydroxy-derivative, out of ten possible isomers, identical with alizarin—

$$\underset{\text{Dibromanthraquinone.}}{C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_2Br_2} + 2KOH = \underset{\text{Alizarin.}}{C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_2(OH)_2} + 2KBr.$$

Manufacture of Alizarin.—The somewhat costly process of Graebe and Liebermann was soon relinquished in favour of a method discovered simultaneously by these two chemists and by Perkin. The anthraquinone is heated with fuming sulphuric acid (containing 40 per cent. of sulphur trioxide) to 160°, and is converted into anthraquinone-β-monosulphonic acid.[1] The

[1] In the presence of a very small amount of mercury sulphonation of anthraquinone takes place only at the α-position. In the absence of mercury only the β-position is attacked.

sodium salt is then prepared by neutralisation of the sulphonic acid with sodium carbonate—

$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4 + H_2SO_4 = \underset{\text{Anthraquinone-}\beta\text{-sulphonic acid.}}{C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_3{\cdot}SO_3H} + H_2O.$$

The crystals of the sodium salt are fused in a closed vessel with caustic soda and a little potassium chlorate. The chlorate furnishes the necessary oxygen required by the reaction—

$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_3SO_3Na + NaOH + 2O$$
$$= \underset{\text{Alizarin.}}{C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_2(OH)_2} + Na_2SO_3.$$

The alizarin, present as the deep violet sodium compound, is extracted with water, in which it readily dissolves, and digested with milk of lime.

$$\underset{\text{Sodium alizarate.}}{C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_2(ONa)_2.}$$

Insoluble calcium alizarate is thus formed, whilst the impurities remain in solution. The calcium alizarate is filtered and decomposed with hydrochloric acid, whereby the alizarin is precipitated in the form of a light brown, amorphous powder. It comes into commerce mixed with water in the form of a paste containing 10 or 20 per cent. of alizarin. In order to obtain alizarin in crystals, it may be sublimed or crystallised from cumene. It forms ruby-red prisms, which melt at 290° and sublime without decomposition.

EXPT. 202.—The formation of alizarin from anthraquinone sulphonic acid may be shown on a small scale in the following way. Fuse in a hard glass tube a little sodium β-anthraquinone sulphonate with a little powdered caustic soda and a crystal of potassium chlorate until a violet-coloured mass is obtained. The test-tube should be turned round over the flame during the fusion. When cool, the melt of sodium alizarate is extracted with water, in which it dissolves with a deep violet colour. On the addition of acid the insoluble alizarin is precipitated as a buff-coloured powder.

Alizarin is insoluble in water, but dissolves in the caustic alkalis with a violet colour, forming alizarates of sodium and potassium. Many of the metallic compounds are insoluble and are differently coloured. The aluminium alizarate is bright red, the ferric salt violet, and the chromic compound has a chocolate colour. A solution of sodium alizarate poured into a solution of one of the above metallic salts precipitates the insoluble alizarate, called a *lake*, and when washed and dried it is used as a pigment.

EXPT. 203.—Make moderately strong solutions of alum, ferric chloride, a mixture of alum and a few drops of ferric chloride and also chromic chloride in separate cylinders, and pour into each a little alizarin dissolved in a few c.c. of caustic soda solution. The metallic oxide precipitated by the alkali combines with the alizarin to form an insoluble lake (or metallic alizarate) which has a different colour in each case.

The formation of lakes explains the application of alizarin in the dyeing of cotton. Alizarin is insoluble in water, and has, moreover, no natural affinity for vegetable fibres. In order to attach it to cotton, the cloth or yarn is first impregnated with a salt, usually the acetate, of aluminium, iron, or chromium. It is then submitted to the action of heat, whereby the acetic acid is driven off and the metallic oxide left attached to the fibre. The cotton is said to be mordanted (p. 445). When steeped in water containing alizarin in suspension, the oxide unites with the colouring matter, and the cotton is permanently dyed. By using different mordants or mixtures of them, a variety of tints is produced. In printing cotton cloth, the metallic salt is thickened with gum, or starch paste, and printed on the fabric, after which it is decomposed by passing over steam-heated iron plates. The cloth is then washed and dyed in alizarin, when the colour adheres to the pattern printed with the metallic salt.

EXPT. 204.—Cloth mordanted with stripes of different metallic oxides when moistened and left in a beaker of hot water containing a little alizarin in suspension takes up the dye and after a few minutes each stripe, according to the nature of the mordant, exhibits a different colour.

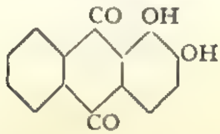
Structure of Alizarin.—Alizarin has been prepared synthetically

by heating together a mixture of phthalic anhydride and catechol with sulphuric acid to 150°

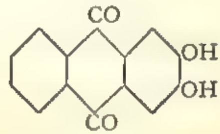
$$C_6H_4\begin{array}{c}\diagup CO \diagdown \\ \diagdown CO \diagup\end{array}O + C_6H_4(OH)_2 = C_6H_4\begin{array}{c}\diagup CO \diagdown \\ \diagdown CO \diagup\end{array}C_6H_2(OH)_2 + H_2O.$$

It follows that the two hydroxyl groups are attached to adjacent carbon atoms in the same nucleus, but leaves undecided which of the following two structures, I. or II., is correct.

I.



II.



The true formula has been ascertained in the following way. If phthalic anhydride and phenol are heated with sulphuric acid two monohydroxyanthraquinones are formed, each of which can be converted into alizarin. This could only happen if the hydroxyl groups occupy the α-β-positions as represented in Formula I., which is the generally accepted formula for alizarin.

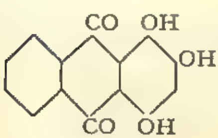
In addition to alizarin a number of trihydroxyanthraquinones are prepared and used as dyes.

Purpurin, 1-2-4-*Trihydroxyanthraquinone*, accompanies alizarin in madder, but is now prepared synthetically by oxidising alizarin with sulphuric acid and manganese dioxide.

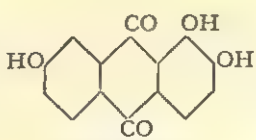
Anthrapurpurin, 1-2-7-*Trihydroxyanthraquinone*, is obtained from the anthraquinone-1-2′-disulphonic acid by fusion with caustic soda and potassium chlorate in the same manner that alizarin is obtained from the monosulphonic acid.

Flavopurpurin, 1-2-6-*Trihydroxyanthraquinone*, is formed like anthrapurpurin from 1-6-anthraquinone-disulphonic acid.

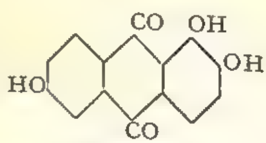
The structural formulæ of the three compounds is represented as follows :—



Purpurin.



Anthrapurpurin.



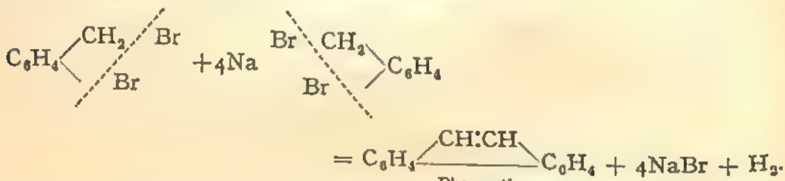
Flavopurpurin.

All these compounds dye a brilliant red with alumina mordants, but of a slightly yellower shade than alizarin. They are the chief constituents of commercial alizarin sold under the name of *yellow shade* alizarin.

It is an interesting fact that among the ten dihydroxyanthraquinones and the numerous trihydroxy-compounds which have been prepared, only those can be used as dyes, which contain the two hydroxyl groups in the α-β-position in the same nucleus.

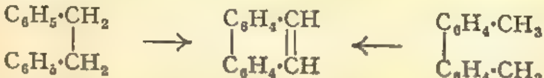
Phenanthrene, $C_{14}H_{10}$, is isomeric with anthracene, and accompanies it in coal-tar. It is present in considerable quantity in crude anthracene, and is removed as already described (p. 547); but it has no commercial value. It crystallises in colourless needles, melts at 99° and distils at 340°. Its interest is mainly derived from its relation to anthracene and to morphine.

Phenanthrene has been prepared synthetically by boiling *o*-bromobenzyl bromide with metallic sodium, which also yields anthracene hydride in the manner already explained (p. 550). The phenanthrene hydride, which is probably first formed in the reaction, loses hydrogen and gives phenanthrene—



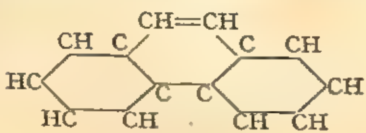
Phenanthrene.

The structure of phenanthrene is further determined by its formation from dibenzyl and *o*-ditolyl by passing them through red-hot tubes, and in other ways—



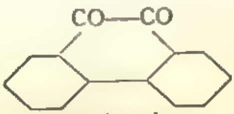
Dibenzyl. Phenanthrene. Ditolyl.

Phenanthrene must therefore be regarded as a derivative of diphenyl in which the two ortho-positions of the nuclei are linked by the group CH:CH—

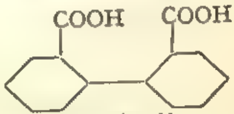


Phenanthrene.

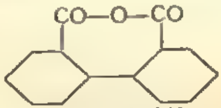
Phenanthrene forms a diketone, or *phenanthraquinone*, $C_{14}H_8O_2$, on oxidation with chromic acid, which bears a close resemblance to β-naphthaquinone. It crystallises in orange needles, which melt at 198°; it has no smell, and is not volatile in steam. It is reduced by sulphurous acid, forms a dioxime and a bisulphite compound. When phenanthraquinone is further oxidised with chromic acid, it is converted into a dibasic acid, *diphenic acid*, $C_{14}H_{10}O_4$, which forms an anhydride. The formation of the anhydride recalls that of naphthalic anhydride (p. 545). The formulæ of these compounds are represented as follows—



Phenanthraquinone.



Diphenic acid.



Diphenic anhydride.

Phenanthraquinone combines with *o*-diamines in presence of acetic acid and forms yellow, crystalline substances, a reaction which serves to distinguish *o*-diamines from other amines (p. 430)—

$$\begin{array}{l} C_6H_4{\cdot}CO \\ | \qquad\quad | \\ C_6H_4{\cdot}CO \end{array} + \begin{array}{l} H_2N \\ H_2N \end{array}\!\!>C_6H_4 = \begin{array}{l} C_6H_4C{:}N \\ | \qquad\quad | \\ C_6H_4C{:}N \end{array}\!\!>C_6H_4 + 2H_2O.$$

When phenanthraquinone is boiled with a concentrated solution of caustic alkali rearrangement takes place with formation of a salt of diphenylene glycollic acid. This is similar to the benzil-benzilic acid transformation (p. 477).

Diphenylene glycollic acid.

Fluorene, *diphenylene methane*, $C_{13}H_{10}$, a hydrocarbon present in coal-tar, can be made by reducing **fluorenone** or *diphenyleneketone*, $C_{13}H_8O$, which results from the dry distillation of the calcium salt of diphenic acid.

QUESTIONS ON CHAPTER XXXVIII

1. Explain the commercial process for obtaining anthracene. What substances accompany it in coal-tar, and how are they removed?

2. Give an account of the properties of anthracene. What conclusions would you draw as to its structure from a consideration of the chemical properties of anthracene?

3. Describe one synthesis of each of the following: (1) anthracene, (2) anthracene hydride, (3) anthraquinone. From these syntheses describe the relation of the three compounds by means of structural formulæ.

4. In what respects do the central carbon groups of anthracene differ from the other carbon groups? Indicate by numbers or letters their relative positions in the isomeric di-derivatives of anthracene.

5. Discuss the structure of anthraquinone. How is it obtained in the pure state? Why is it called a quinone, and is the appellation a correct one?

6. Describe the production of alizarin. How is the dye applied to cotton? What is the meaning of the terms *lake* and *mordant*?

7. How has the structure of alizarin been ascertained? What other derivatives of anthraquinone are used as dyes?

8. Give an account of the phenanthrene and some of its more important derivatives.

PART III

COMPLEX COMPOUNDS

CHAPTER XXXIX

HETEROCYCLIC COMPOUNDS

FURFURANE, THIOPHENE, PYRROLE, ETC.

Heterocyclic Compounds.—The term heterocyclic is applied to ring compounds, not composed wholly of carbon atoms, like those which have been described in preceding chapters (homocyclic compounds); but in which one or more of the links in the closed chain are supplied by other polyvalent elements, such as oxygen, sulphur, or nitrogen. We have already met with examples of this type of compound in the lactones (p. 320) and the anhydrides of dibasic acids (p. 350), in which oxygen is an element in the ring; also in succinimide and phthalimide (p. 498), which contain an atom of nitrogen, and in piperazine (p. 208a), which has two atoms of nitrogen in the ring; uric acid and its numerous derivatives (Chapter XLI) form condensed, or double rings, consisting of a carbon and nitrogen skeleton. Such heterocyclic compounds are very common, and their synthesis forms an interesting chapter in recent research.

It would cover too much ground, and exceed the scope of the present volume, to give even a summary of all the different known classes of heterocyclic compounds. Some idea of their number and variety may be gathered from the examples which are given below. It should be pointed out that the most common kinds of ring compounds are those consisting of nuclei of 5 and 6 atoms, or condensed nuclei of the type of naphthalene and anthracene. Ring compounds composed of a larger or smaller number of atoms are less common.

An explanation of these facts has already been indicated, and is based upon stereochemical considerations (p. 320). We have selected for illustration three examples of heterocyclic compounds containing oxygen, sulphur, and nitrogen in a ring skeleton of

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COMPLEX COMPOUNDS

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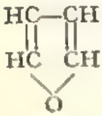
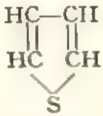
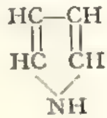
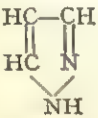
5 atoms. They are known as **furan, thiophene,** and **pyrrole,** and their structures are usually expressed by the following formulæ—

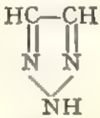

Furan.

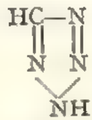

Thiophene.


Pyrrole.

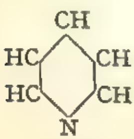
Pyrazole, Triazole, and **Tetrazole** represent 5-atom rings, containing 2, 3, and 4 nitrogen atoms—

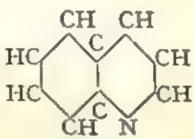

Pyrazole.

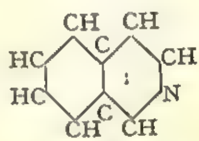

Triazole.


Tetrazole.

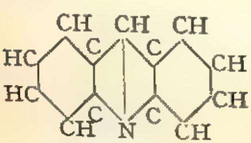
Examples of 6-atom rings are furnished by **pyridine, quinoline,** and **isoquinoline,** which may be compared with benzene and naphthalene, wherein an atom of nitrogen replaces one of the CH groups of the ring–

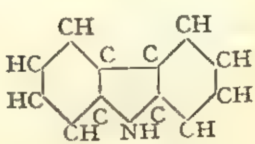

Pyridine.


Quinoline.


Isoquinoline.

These three substances may be regarded as the parent compounds of the **alkaloids**, which are described in the succeeding chapter. **Acridine**, which corresponds to anthracene in structure, and **carbazole,** which is a dibenzopyrrole, or condensed nucleus of pyrrole and benzene, are other well-known examples of heterocyclic compounds.


Acridine.

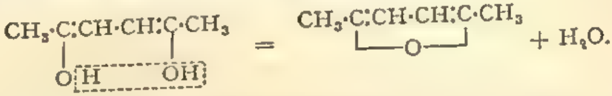

Carbazole.

The structure and properties of the more important of these compounds will be discussed in the following pages.

Furan, C_4H_4O, is found in the distillate of pine-wood tar. It is also obtained by distilling the barium salt of pyromucic acid (obtained by heating mucic acid) with soda-lime—

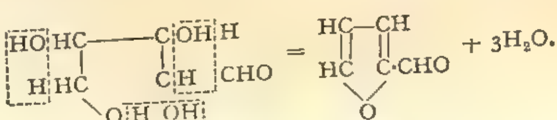
$$\underset{\text{Pyromucic acid.}}{C_4H_3O{\cdot}COOH} = \underset{\text{Furan.}}{C_4H_4O} + CO_2.$$

An interesting synthesis of furan derivatives is effected by the action of dehydrating agents, like acetyl chloride, on diketones (known as 1-4-diketones from the number of carbon atoms which separate the oxygen atoms) of the general formula $R{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}R$. This reaction is explained by supposing a tautomeric change (p. 330) to take place in the structure of the diketone, which then loses a molecule of water. Acetonyl acetone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, gives dimethylfuran—



Furan is a liquid which boils at 32°. No hydrogen is evolved when sodium is added to it, nor does it combine with hydroxylamine or phenylhydrazine. The oxygen is therefore not present as a hydroxyl, or ketone group, which is in agreement with the theory of a ring structure. The vapour of furan reddens a pine shaving moistened with hydrochloric acid, and it gives a violet colour with isatin, or with phenanthraquinone dissolved in strong sulphuric acid (see reactions for thiophene and pyrrole).

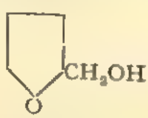
Furfural, *Furfuraldehyde,* $C_4H_3O{\cdot}CHO$.—The most important derivative of furan is the aldehyde, furfural, which is found in the distillate when the pentoses are boiled with strong hydrochloric acid. The reaction is used for the quantitative estimation of pentoses in the following manner: Phenylhydrazine is added to the distillate, and the solid phenylhydrazone of furfural is then collected and weighed—



Pentose. Furfural.

Furfural is now a commercial product and is made in large quantities in the United States by heating the hulls of oats and corn cobs with 5 per cent. sulphuric acid under steam pressure. It is used as a solvent for leather dyes and its derivatives are employed in the preparation of perfumes, succinic and citric acids, as a fungicide, for the production of phenol aldehyde resins (see p. 461), and in the manufacture of dyes. When freshly distilled and pure, it is a colourless liquid with an agreeable smell, which boils at 162°; but it soon darkens on standing. It possesses in a very marked degree the characteristics of an aromatic aldehyde.

It yields *furfuralcohol* on reduction, and *pyromucic acid* by oxidation—



Furfuralcohol.

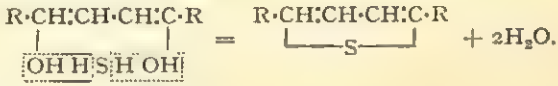
Pyromucic acid.

With ammonia it forms *hydrofurfuramide*, corresponding to hydrobenzamide (p. 476), and *furoin* with potassium cyanide, corresponding to benzoin (p. 477); it gives Perkin's (p. 501) and Claisen's reactions (p. 477), and forms furfuraldehyde green with dimethylaniline and zinc chloride (p. 517). A delicate rest for furfural is to expose to its vapour a piece of filter paper dipped in a solution of aniline hydrochloride, which immediately turns pink.

Thiophene, C_4H_4S.—The blue colour, or indophenine reaction (p. 388), which coal-tar benzene (as distinguished from synthetic benzene from benzoic acid or aniline) gives with isatin dissolved in strong sulphuric acid, was traced by V. Meyer to the presence of a small quantity (about 0·5 per cent.) of a liquid, to which he gave the name of thiophene.

Thiophene has since been obtained by a variety of synthetic processes, which for the most part consist in heating mono- and di-basic acids, or alcohols containing 4 carbon atoms with phosphorus sulphide. Sodium succinate and phosphorus trisulphide, when distilled, afford the best yield of thiophene. Its homologues are obtained from the 1-4-diketones (which yield furans) by heating them with phosphorus sulphide. The explanation of the

course of the reaction is similar to that given in describing the process for obtaining furan derivatives, the sulphide of phosphorus furnishing in the present instance the necessary hydrogen sulphide—

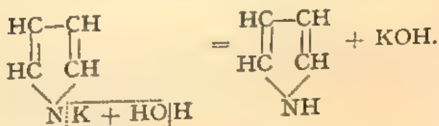


Thiophene is a colourless liquid with a faint smell resembling benzene, and boils at about the same temperature as benzene (84°).

Thiotolene, or methylthiophene, and *thioxene*, or dimethylthiophene, are found in small quantities in the toluene and xylene fractions of coal-tar naphtha.

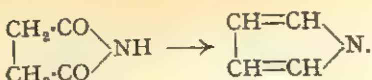
All these substances possess the distinctive benzenoid characters of ring compounds, viz. the property of forming sulphonic acids and nitro-derivatives with sulphuric and nitric acids. Moreover, the side-chains of the alkyl thiophenes are oxidised, like the benzene homologues, to carboxyl groups, and form acids.

Pyrrole, C_4H_5N, is found in small quantities in coal-tar and to a larger extent in *bone-oil* or Dippel's oil. Dippel's oil, so called from its discoverer, who used it as a medicine, is obtained by distilling bones. The glutin (p. 599) of the bone is decomposed and converted into volatile nitrogenous substances, the majority of which possess basic characters. Pyrrole is separated from the black, oily distillate by conversion into the solid potassium pyrrole, C_4H_4NK, which it forms on boiling with solid caustic potash. The potassium compound is separated and decomposed by water into pyrrole and potash—



Potassium pyrrole. Pyrrole.

Pyrrole is also obtained by distilling succinimide with zinc dust—



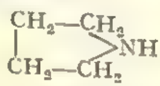
Succinimide. Pyrrole.

The homologues of pyrrole are prepared from the same class of diketones, which yield furan and thiophene compounds, by heating them with ammonium acetate, and the reaction may be explained in a similar fashion—

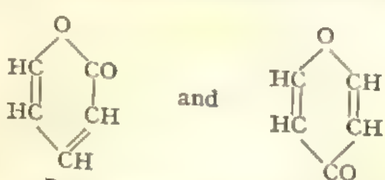
Pyrrole is a colourless liquid, which boils at 131°. It received its name from the property of reddening a pine shaving moistened with hydrochloric acid (πυῤῥός, flame-coloured). It possesses the characters of a secondary amine and forms a nitrosamine and an acetyl derivative; but it is a very weak base and also a very weak acid. When the acid solution is warmed, it deposits a red, amorphous powder, known as *pyrrole red*.

Iodole, *Tetriodopyrrole,* $C_4I_4 \cdot NH$, is obtained by the action of iodine and potash on pyrrole, and, being without smell and a strong antiseptic, is used as a substitute for iodoform.

On reduction with sodium and alcohol, pyrrole yields a strongly basic secondary amine, pyrrolidine—



Pyrones, are heterocyclic compounds containing one oxygen atom in the ring and one carbonyl group, and are of two kinds, viz. α- and γ-pyrones—

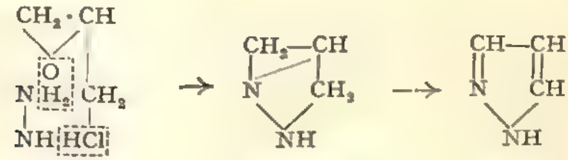


α-Pyrone. γ-Pyrone.

Coumarin (p. 504) is a derivative of the α-pyrones. The γ-pyrones occur in various natural colouring matters. Strangely enough, the γ-pyrones do not give the characteristic reactions of ketones, but their chief interest lies in the fact that although they contain no nitrogen, they are basic, and form salts with mineral acids; these salts are called *oxonium* salts, and are usually assumed to contain quadrivalent oxygen.

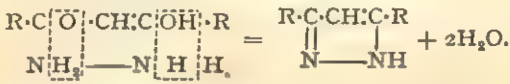
Pyrazole, $C_3H_4N_2$, has only been obtained by direct synthesis. It is formed by the action of hydrazine on epichlorhydrin in presence of zinc chloride, when condensation occurs and a ring compound

is formed. At the same time two atoms of hydrogen are removed by the reducing action of the hydrazine, which is thereby converted into ammonia—



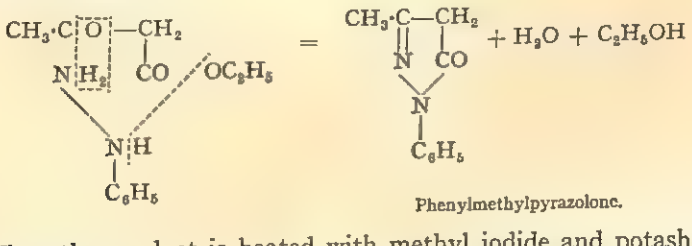
Epichlorhydrin + hydrazine. Intermediate product. Pyrazole.

Many of the derivatives of pyrazole are obtained by the action of hydrazine or its derivatives on 1-3-diketones, of the general formula R·CO·CH$_2$·CO·R. The diketone undergoes tautomeric change and condensation in the following way—



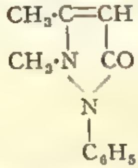
Pyrazole is a crystalline compound which melts at 70° and boils at 187° and possesses the properties of a weak base.

Antipyrine.—The most important of the pyrazole derivatives is antipyrine, which has a very extensive use in medicine as a febrifuge. It is obtained by heating together acetoacetic ester and phenylhydrazine. Condensation occurs, and the product, which contains one of the carbon atoms in the form of a ketone group, is known as phenylmethylpyrazolone. It is formed in the following manner—



Phenylmethylpyrazolone.

When the product is heated with methyl iodide and potash, a tautomeric change occurs in the position of one hydrogen atom, which wanders to the doubly-linked nitrogen and is replaced by a methyl group—



Formula of Antipyrine.

Antipyrine is a colourless, crystalline compound, which melts at 113° and dissolves in water. It is a base, and forms soluble salts. The aqueous solution gives a red colour with ferric chloride and a bluish-green with nitrous acid.

PYRIDINE, QUINOLINE, ISOQUINOLINE

Pyridine, C_5H_5N.—Pyridine is found in the light-oil distillate from coal-tar, from which it is separated by treatment with sulphuric acid in the ordinary course of purification. If an alkali is added to the acid liquid, a dark-coloured oil separates, containing pyridine and its homologues, together with quinoline, isoquinoline, aniline, etc., the constituents of which may be partially separated by fractional distillation. Pyridine and its homologues, together with quinoline, are also present in considerable quantities in bone-oil (p. 565).

Pyridine is a colourless liquid, which boils at 115° and mixes in all proportions with water. It has a strongly alkaline reaction towards litmus, and possesses a peculiar smell, which is characteristic of both pyridine and quinoline and many of their homologues. Pyridine is very indifferent to most reagents. It is unaffected by boiling strong nitric acid or chromic acid. Sulphuric acid only attacks it at a high temperature, forming a sulphonic acid. In the same way the halogens have little action on pyridine under conditions which in the case of benzene give rise to substitution products. With strong reducing agents, like strong hydriodic acid, nitrogen is eliminated in the form of ammonia, and the remainder of the molecule is reduced to pentane—

$$\underset{\text{Pyridine.}}{C_5H_5N} + 5H_2 = \underset{\text{Pentane.}}{C_5H_{12}} + NH_3.$$

Pyridine is a base, and forms salts with acids, which are usually

soluble in water. It gives also a yellow, crystalline double salt with platinic chloride like other organic bases.

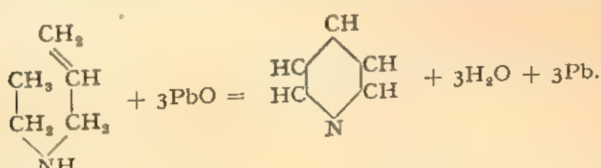
$C_5H_5N{\cdot}HCl$ — Pyridine hydrochloride. $(C_5H_5N{\cdot}HCl)_2PtCl_4$. — Pyridine platinochloride.

It is, moreover, a tertiary base, for it neither combines with acetyl chloride to form an acetyl derivative, nor with nitrous acid to form a nitrosamine; but it unites with methyl iodide, and gives the quaternary ammonium compound, or pyridinium methyl iodide, $C_5H_5N{\cdot}CH_3I$, which is a crystalline compound.

EXPT. 205.—Warm a mixture of equal volumes of pyridine and methyl iodide; a reaction sets in and the liquid boils. When cold, the crystalline quaternary compound is deposited.

Structure of Pyridine.—The stability of pyridine towards reagents, and the fact that the alkyl pyridines are oxidised to pyridine carboxylic acids (p. 571), is an indication that we are dealing with a ring compound, and this view is supported by numerous syntheses, of which the following are the most instructive.

Allylethylamine passed over heated lead oxide gives pyridine—



Allylethylamine. Pyridine.

More important from the point of view of structure is the relation of pyridine to piperidine or hexahydropyridine, $C_5H_{11}N$. Piperidine is a constituent of black pepper (p. 581), and is a liquid with a strong ammoniacal smell. It gives pyridine on oxidation with strong sulphuric acid, or nitrobenzene; and pyridine, on the other hand, is reduced to piperidine by the action of sodium on the alcoholic solution—

$$\underset{\text{Pyridine.}}{C_5H_5N} \rightleftarrows \underset{\text{Piperidine.}}{C_5H_{11}N}.$$

The relation of the two substances is that of benzene to cyclohexane or hexahydrobenzene (p. 383).

Now piperidine has been synthesised by the dry distillation of pentamethylenediamine hydrochloride (p. 208a)—

$$H_2C\begin{cases} CH_2\cdot CH_2\cdot NH\,|\,HHCl \\ CH_2\cdot CH_2\cdot|\,NH_2 \end{cases} = H_2C\begin{cases} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{cases} NH + NH_4Cl$$

Piperidine.

Also, by heating an aqueous solution of chloramylamine—

$$H_2C\begin{cases} CH_2\cdot CH_2\cdot NH_2 \\ CH_2\cdot CH_2\cdot Cl \end{cases} = H_2C\begin{cases} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{cases} NH\cdot HCl.$$

Chloramylamine.

It follows, therefore, that pyridine is a ring compound composed of a skeleton of 5 carbon atoms and 1 nitrogen atom. By attaching a hydrogen atom to each carbon atom the formula C_5H_5N is arrived at. We may dispose of the fourth bond of carbon and the third bond of nitrogen, which remains unaccounted for, by adopting the alternate double linkage of Kekulé, which was suggested by Körner, or a para-bond as shown below, or by accepting the centric arrangement proposed by Bamberger.

Körner's formula.

Dewar's formula.

Centric formula.

Isomerism of Pyridine Derivatives.—The number of mono-derivatives which would be anticipated from a compound of the structure of pyridine is three; for the substance may be compared with a mono-derivative of benzene, inasmuch as one position in the ring, viz. that occupied by the nitrogen atom, is differentiated from the rest, and this is in perfect agreement with the experimental facts. The three positions are indicated by the Greek letters α, β, and γ.

The distinction between α, β and γ methyl pyridines can be settled by disrupting the compounds by energetic reduction with strong hydriodic acid (p. 568). The α-compound gives *n*-hexane, the others give branched paraffins.

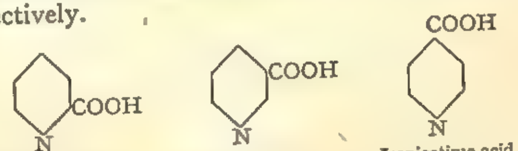
There are three methyl pyridines, three hydroxypyridines, three pyridine-carboxylic acids, etc.

Homologues of Pyridine.—The three methyl pyridines are known as **picolines,** the dimethylpyridines as **lutidines,** and the trimethylpyridines as **collidines.** They possess the general characters of pyridine. On oxidation, the side-chains are converted into carboxyl groups and mono-, di-, and tri-basic acids are formed after the manner of the methyl derivatives of benzene (p. 396); but the acids are necessarily weaker, for they are partly neutralised by the basic character of the nucleus.

There are various means of obtaining the homologues of pyridine. They occur in coal-tar and bone-oil, but they are also formed synthetically. An interesting process for obtaining the α-alkylpyridines is the action of heat on quaternary alkylpyridinium iodides. Pyridine methyl iodide heated to 300° gives α-picoline hydriodide. The method recalls the conversion of methylaniline into toluidine (p. 428).

Pyridinium methyl iodide. α-Picoline hydriodide.

Pyridine-carboxylic Acids.—The α-, β-, and γ-monocarboxylic acids of pyridine are known as **picolinic, nicotinic,** and **isonicotinic** acids, respectively.

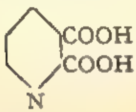


Picolinic acid. Nicotinic acid. Isonicotinic acid.

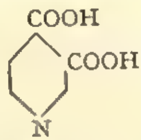
They can be obtained by the oxidation of the respective alkyl pyridines, as already mentioned. Of greater interest is their appearance among the products of oxidation of certain alkaloids. Thus, *coniine* (p. 581) yields picolinic acid, whereas *nicotine* forms nicotinic acid. For this reason the identification of the three acids, which is easily effected from a determination of their melting-points and from other specific characters, is often of fundamental importance in arriving at the structure of the alkaloid under examination. Picolinic acid melts at 136°. It loses carbon dioxide when heated, and gives an orange colour with ferrous sulphate. The colour reaction with ferrous sulphate and the loss of carbon

dioxide on heating are characteristic of all the pyridine derivatives containing carboxyl in the α-position. Nicotinic acid melts at 229° and isonicotinic acid at 304°. They are all crystalline substances, which dissolve more or less readily in water.

Quinolinic and Cinchomeronic Acids, $C_5H_3N(COOH)_2$, are pyridine-dicarboxylic acids. Quinolinic acid, or pyridine-αβ-dicarboxylic acid, is obtained by oxidising quinoline (see below); cinchomeronic acid, or pyridine-βγ-dicarboxylic acid, by oxidising isoquinoline (p. 576).



Quinolinic acid.



Cinchomeronic acid.

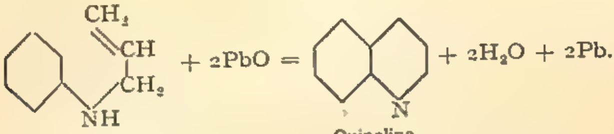
Both acids give anhydrides like phthalic acid by boiling with acetic anhydride; but if heated alone they lose carbon dioxide. Quinolinic acid is readily converted into nicotinic acid, whereas cinchomeronic acid forms, though at a much higher temperature, isonicotinic acid.

Quinoline, C_9H_7N, was originally obtained by Gerhardt (1842) by distilling quinine, strychnine, and other alkaloids with caustic potash. The oil which distilled received the name of quinolein, which was changed to quinoline. Shortly afterwards (1846) Anderson isolated the same compound and many of its homologues from bone-oil. It is also present in coal-tar.

The most convenient source of quinoline is the synthetic method discovered by Skraup, to be presently described. Quinoline is a colourless liquid with a smell resembling that of pyridine; but it differs from pyridine in not mixing with water, and it boils at a much higher temperature (236°). In chemical properties the two substances correspond closely. Quinoline is a tertiary base, and forms well-defined salts. The acid chromate, $(C_9H_7N)_2H_2CrO_4$, is sparingly soluble in water, and is precipitated in the form of yellow needles on the addition of potassium chromate to a solution of a salt of quinoline.

Structure of Quinoline.—The structure of quinoline is derived from its synthesis, and from the nature of its decomposition products. It is obtained by passing the vapours of allylaniline over

heated lead oxide, a reaction which recalls the formation of pyridine from allylethylamine (p. 569).

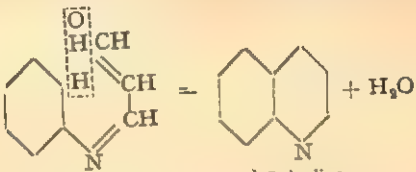


Allylaniline. Quinoline.

Skraup's Synthesis consists in heating a mixture of aniline, glycerol, strong sulphuric acid, and nitrobenzene. The action is a vigorous one, and when complete the product is made alkaline and distilled in steam. The quinoline distils and is purified by fractionation. The process may be explained as follows. The glycerol is converted into acrolein, which forms acrylaniline with the aniline. The nitrobenzene then oxidises the acrylaniline to quinoline—

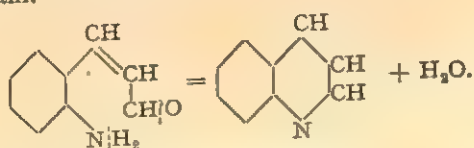
1. $C_6H_5NH_2 + OCH{\cdot}CH{:}CH_2 = \underset{\text{Acrylaniline.}}{C_6H_5N{:}CH{\cdot}CH{:}CH_2} + H_2O.$

2.



Acrylaniline. Quinoline.

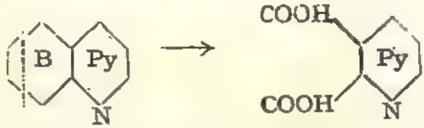
Baeyer has also synthesised quinoline in a very simple and suggestive manner by the reduction of *o*-nitro-cinnamic aldehyde. The nitro-compound on reduction yields the corresponding amino-compound, which undergoes condensation with the aldehyde group in the side-chain.



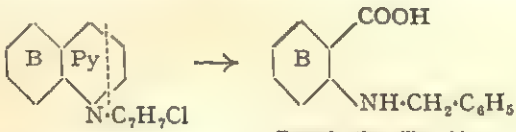
o-Aminocinnamic aldehyde. Quinoline.

A clear insight into the structure of quinoline is afforded by

the production of quinolinic acid (p. 572) when quinoline is boiled with potassium permanganate. The reaction is precisely analogous to the formation of phthalic acid from naphthalene. In this case, what may be termed the benzene nucleus (B) is destroyed, and the pyridine nucleus (Py) remains—



By converting quinoline into a quaternary ammonium compound with benzyl chloride, the pyridine nucleus is weakened, and when the product is submitted to oxidation the pyridine nucleus is destroyed and the benzyl derivative of anthranilic acid is formed—



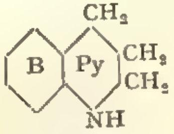
Benzylanthranilic acid.

It follows, therefore, that quinoline contains a benzene and pyridine nucleus, and its structure, like that of naphthalene, may be interpreted by the aid of Körner's formula—

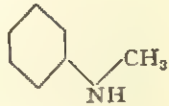
Körner's formula.

The same difficulty arises in formulating quinoline as exists in the cases of benzene and naphthalene. Until the point is definitely settled it will be sufficient to use simple hexagonal structures without double bonds.

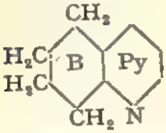
Quinoline, like the naphthalene compounds, gives two tetrahydro-derivatives on reduction. One compound, in which the pyridine nucleus is reduced, resembles methylaniline in a very remarkable degree, whilst the second compound, in which the benzene nucleus is reduced, corresponds very closely with xylidine. A reference to the paragraph relating to naphthalene will make these points clear (p. 536).



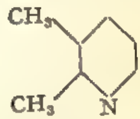
Py-tetrahydroquinoline.



Methylaniline.

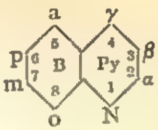


B-Tetrahydroquinoline.

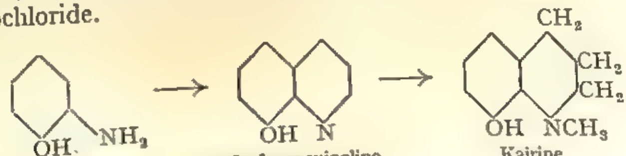


Xylidine.

Isomerism of Quinoline Derivatives.—The number of isomeric mono-derivatives of quinoline is obviously very large. They are distinguished by lettering the three positions of the pyridine nucleus with the Greek letters α, β, γ, and indicating the four positions of the benzene nucleus by *ortho*, *meta*, *para*, and *ana*, or by simply numbering the positions in the two nuclei and attaching the symbols B and Py to distinguish them.



Derivatives of Quinoline.—Skraup's reaction has a general application, *i.e.* it can be employed not only for converting aniline into quinoline, but aromatic amino-compounds in general into quinoline derivatives. It necessarily follows that such quinoline derivatives are substituted in the benzene nucleus. Thus, *o*-aminophenol, when heated with glycerol, sulphuric acid, and nitrobenzene, is converted into hydroxyquinoline. When hydroxyquinoline is reduced with tin and hydrochloric acid, it gives Py-tetrahydro-B-hydroxyquinoline, and the product, when methylated with methyl iodide, yields **kairine**, which was formerly much used in medicine as an antipyretic. Kairine is a crystalline base, and forms a soluble hydrochloride.

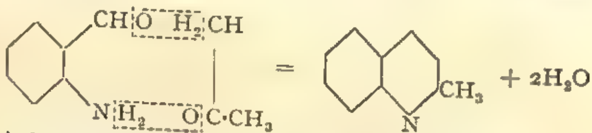


o-Aminophenol. B-*o*-hydroxyquinoline. Kairine.

When *p*-methoxyaniline is submitted to a similar process, it gives methoxyquinoline, and the tetrahydro-derivative has also been used in medicine under the name of *thalline*.

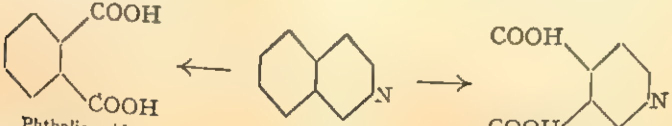
The drugs *plasmoquin* and *atebrin*, used in the treatment of malaria, belong to a group of quinoline and acridine derivatives containing a side-chain of the general form $-NH(CH_2)_nN(C_2H_5)_2$.

In addition to Skraup's reaction many other synthetic processes are available for obtaining quinoline derivatives. The action of ketones and aldehydes on *o*-aminobenzaldehyde affords a simple example. Acetone forms α-methyl quinoline (quinaldine)—



o-Aminobenzaldehyde. Acetone. α-Methyl quinoline (Quinaldine).

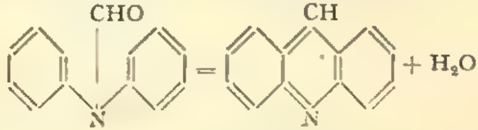
Isoquinoline, C_9H_7N, is isomeric with quinoline, and was first separated by Hoogewerff and van Dorp from the crude coal-tar quinoline by fractional crystallisation of the sparingly soluble sulphate. It is a colourless, crystalline substance, which melts at 21° and boils at 237°. It resembles quinoline in properties. Isoquinoline has increased in interest since its recognition as the parent substance of several alkaloids, such as *berberine*, the alkaloid of barberry, and the alkaloids *narcotine*, *papaverine*, and *hydrastine*, which accompany morphine in opium. Isoquinoline has been synthesised in several ways; but its structure is most clearly and simply determined by the products which it yields on oxidation. It is broken up into phthalic acid and cinchomeronic acid (p. 572) in the following way—



Phthalic acid. Isoquinoline. Cinchomeronic acid.

In one case the pyridine nucleus is destroyed and phthalic acid is formed; in the other, it is the benzene nucleus which suffers extinction and cinchomeronic or βγ-pyridine-dicarboxylic acid is produced.

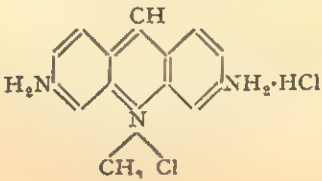
Acridine, $C_{13}H_9N$, is found in crude coal-tar anthracene. Its structure (p. 562) is proved by its synthesis from formyl-diphenylamine and zinc chloride. Its solutions are strongly fluorescent.



Acridine.

Moreover, on oxidation with permanganate it forms quinoline-α-β-dicarboxylic acid. Acridine is the mother substance of several important colouring matters and valuable drugs.

Acriflavine, the methochloride of diaminoacridine, is a valuable antiseptic—



Acriflavine.

Carbazole, $C_{12}H_9N$, accompanies anthracene in anthracene oil, and is separated from the crude anthracene by distillation with a small quantity of caustic potash, which retains the carbazole in the form of the potassium compound (p. 547). This compound of carbazole corresponds with that of pyrrole, of which it may in fact be regarded as a derivative (p. 565).

Potassium carbazole.

Like pyrrole also, it gives the red colour with a pine shaving moistened with hydrochloric acid, and a blue colour to a sulphuric acid solution of isatin (p. 566). It has been obtained synthetically by passing diphenylamine through a red-hot tube and in other ways—

$$\underset{\text{Diphenylamine.}}{C_6H_5\diagdown\underset{NH}{}\diagup C_6H_5} = \underset{\text{Carbazole.}}{C_6H_4\diagdown\underset{NH}{}\diagup C_6H_4} + H_2.$$

It is a crystalline compound, possessing feebly basic properties; it melts at 238° and boils at 351°.

Questions on Chapter XXXIX

1. Explain the meaning of *heterocyclic compounds*. Give examples drawn from the aliphatic series. Name some heterocyclic compounds composed of 5 atoms, and give their formulæ.

2. Compare the mode of preparation and properties of furfurane, thiophene, and pyrrole, and their derivatives. Give your reasons for regarding them as ring compounds.

3. What is furfural? How is it most readily obtained? How is it detected and estimated? Compare its properties with those of benzaldehyde.

4. Describe the preparation of antipyrine. What is its relation to pyrazole?

5. Give an account of those properties of pyridine which indicate its ring structure, and any synthesis which points in the same direction.

6. How are the pyridine monocarboxylic acids obtained, and how are they distinguished? Why is their identification of importance?

7. Give an account of the chemical and physical properties of quinoline. Discuss its structure and its relation to pyridine.

8. Describe and explain Skraup's synthesis of quinoline, and name any quinoline derivatives, which have been prepared by this reaction.

9. What is isoquinoline and where is it found? How has its structure been determined? What special interest attaches to it?

10. Compare pyrrole and carbazole in structure and properties.

CHAPTER XL

THE ALKALOIDS

The Alkaloids.—The medicinal properties as well as the poisonous characters of certain plants have long been recognised. Early in the nineteenth century Sertürner, a German apothecary, isolated the active principle of opium in the crystalline form and gave it the name of *morphium*. This discovery quickly led to others, and before long a large number of similar substances had been separated in the pure state from a variety of plants. They possessed basic properties, and were called *alkaloids* or *vegetable bases*; the term alkaloid is used somewhat loosely to denote nitrogenous bases, which have some physiological action, and are generally but not exclusively heterocyclic compounds. Although this description would include compounds like caffeine, which are often classed in medical works as alkaloids, it is more convenient to group them along with uric acid in a separate category (Chap. XLI). Some purely synthetic compounds are recognised, from their properties, as alkaloids. Although the different individuals possess distinctive characters, they have many properties in common. They are optically active and usually lævo-rotatory in solution. They form insoluble compounds with many of the reagents which precipitate the proteins (p. 597), such as tannin, phosphomolybdic acid, and potassium mercuric iodide. They also give amorphous, brown precipitates with iodine solution. They have an alkaline reaction, possess for the most part a bitter taste, and many of them are extremely poisonous. A few of the alkaloids (coniine, nicotine) are liquids, but the majority are crystalline solids, which are insoluble in water, but dissolve in most of the organic solvents, such as ethyl and amyl alcohol, ether, chloroform, etc. The salts, especially the chloride and nitrate, are very soluble in water, and from the solution the insoluble base is precipitated by alkalis. The platinochlorides are yellow, crystalline, and sparingly soluble substances. Most of the alkaloids are tertiary bases and form additive compounds with the alkyl iodides. As a rule they are present in the plant combined with organic acids, such as malic, citric, and lactic acid, or an acid peculiar to the

alkaloid with which it is associated. In cinchona bark, for example, the alkaloids are combined with quinic acid, in aconite with aconitic acid, etc. With the salts of the alkaloids are frequently associated proteins, tannins, resins, essential oils, and other vegetable products, which have to be dealt with in the process of extraction.

For each alkaloid a special process of extraction is employed, and for costly pharmaceutical preparations the estimation of the amount of alkaloid present in the raw material is effected by a recognised and carefully elaborated analytical method. A general scheme for extraction may be briefly indicated. The carefully ground material is digested with water, which dissolves out the salt of the alkaloid, and the solution is then precipitated with an alkali or lime. If the alkaloid is volatile, like coniine, it is separated by distillation in steam; otherwise it is either extracted with a volatile solvent like ether, chloroform, amyl alcohol, etc., or filtered. The solvent in the first case is evaporated or shaken up with acid, which dissolves the alkaloid as the soluble salt; in the second case, the precipitate or its salt is recrystallised. It is seldom that a single alkaloid occurs in the plant; more frequently several are associated, and being chemically related, they are often difficult to separate.

The free alkaloids belong to different classes of compounds, such as amides or esters of organic acids in which the basic character predominates. The amides and esters are separable into a basic and an acid constituent by hydrolysis. The basic portion often contains a hydroxyl, methoxyl, or carboxyl, or all three groups. *Piperine* is an amide, and breaks up on hydrolysis into the base piperidine and piperic acid (p. 581); *atropine* is an ester, and yields the base tropine and tropic acid (p. 583). *Cocaïne* (p. 584) is still more complex. On hydrolysis it gives *ecgonine*, a carboxylic acid derived from *tropine*, together with methyl alcohol and benzoic acid.

In the following pages a short account of some of the better known alkaloids is given, together with their distinctive reactions. They are divided into three classes, viz. those derived from pyridine, others derived from quinoline, and the more complex alkaloids of the opium group, of which morphine is the most important.

Pyridine Alkaloids

Piperine, $C_{17}H_{19}NO_3$.—The fruit and seeds of different kinds of pepper contain from 7 to 9 per cent. of piperine, which is extracted by heating with milk of lime, evaporating to dryness, and extracting the residue with ether.

Piperine is a colourless, crystalline substance which melts at 129°. It breaks up, on hydrolysis with caustic alkalis or acids, into piperidine and piperic acid—

$$\underset{}{C_{17}H_{19}NO_3} + H_2O = \underset{\text{Piperidine.}}{C_5H_{11}N} + \underset{\text{Piperic acid.}}{C_{12}H_{10}O_4}.$$

The structure of piperidine has already been explained (p. 569); that of piperic acid is determined by its conversion into piperonylic acid (p. 494) on oxidation. It is represented by the following formula—

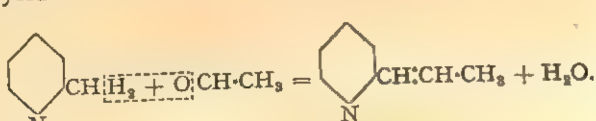
$$CH_2\langle{}^{O}_{O}\rangle C_6H_3\cdot CH{:}CH\cdot CH{:}CH\cdot COOH.$$

Piperic acid.

The structure of piperine is that of an amide of piperic acid in which piperidine is the basic constituent. This agrees with the fact that piperic chloride and piperidine react to form piperine.

Coniine, $C_8H_{17}N$, is the poisonous constituent of hemlock (*Conium maculatum*), to which it imparts its unpleasant smell. The alkaloid is readily obtained by distilling the plant with a solution of caustic soda. The coniine is extracted from the distillate. It is an oil which boils at 167°, and is extremely poisonous. Coniine is α-propylpiperidine. That the side-chain is in the α-position follows from the fact that on energetic reduction with hydriodic acid coniine yields ammonia and *n*-octane. Ladenburg synthesised it as follows.

α-Picoline undergoes condensation with acetaldehyde and forms α-allylpyridine—



α-Picoline. α-Allylpyridine.

alkaloid with which it is associated. In cinchona bark, for example, the alkaloids are combined with quinic acid, in aconite with aconitic acid, etc. With the salts of the alkaloids are frequently associated proteins, tannins, resins, essential oils, and other vegetable products, which have to be dealt with in the process of extraction.

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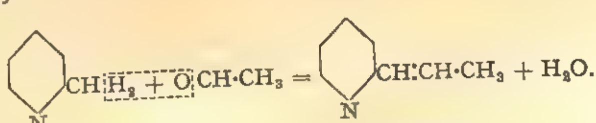
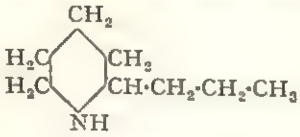


α-Picoline. α-Allylpyridine.

Allylpyridine, on reduction, is converted into α-propylpiperidine—

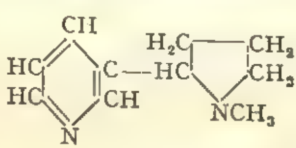


α-Propylpiperidine.

The compound is, however, inactive, whereas coniine is dextro-rotatory. Ladenburg succeeded in resolving the inactive compound into its active components by crystallising the inactive coniine tartrate. The dextro-coniine tartrate is less soluble than the lævo-compound, and is the first to crystallise (p. 372). The resulting α-coniine is identical in every respect with the natural alkaloid.

Nicotine, $C_{10}H_{14}N_2$, is found in combination with malic and citric acids in tobacco leaves in quantities varying from 0·6 to 8 per cent., from which it is removed by distilling with milk of lime. The alkaloid passes into the distillate, which is extracted with ether. Nicotine is an oil which boils at 247°, and is lævo-rotatory. It is very soluble in water, has a strong and disagreeable smell, possesses a burning taste, and is a powerful poison. It is converted into nicotinic acid on oxidation with potassium permanganate or chromic acid (p. 571).

It has recently been prepared synthetically, and both the dextro- and lævo-modifications are known. It is an interesting fact that the natural, lævo-rotatory alkaloid is much the stronger poison. The substance is represented by the following formula—

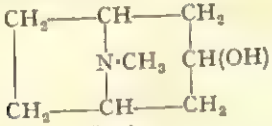


Atropine, $C_{17}H_{23}NO_3$, is a constituent of deadly nightshade (*Atropa belladonna*), henbane (*Hyoscyamus niger*), and thornapple (*Datura strammonium*), in which it is associated with *hyoscyamine*, *hyoscine*, and several other alkaloids. The extracted juice is mixed with caustic potash and shaken up with chloroform. The chloroform solution of the alkaloids is evaporated, and the residue

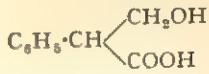
extracted with dilute sulphuric acid, which dissolves the atropine as the sulphate, from which the base is precipitated by alkalis. Atropine crystallises in prisms, which melt at 115°. It is a strong base and forms well-defined salts. Atropine sulphate is used in ophthalmic cases for dilating the pupil of the eye. It is a strong poison. When hydrolysed it breaks up into a base, **tropine,** and an acid, **tropic acid**—

$$\underset{\text{Atropine.}}{C_{17}H_{23}NO_3} + H_2O = \underset{\text{Tropine.}}{C_8H_{15}NO} + \underset{\text{Tropic acid.}}{C_9H_{10}O_3}.$$

When tropic chloride is condensed with tropine, atropine is regenerated. Other acids may replace tropic acid, and the various compounds thus obtained are known as *tropeïnes*. The tropeïne of mandelic acid is used as a substitute for atropine in medicine, and is known as *homatropine*. Tropic acid has been synthesised, and its structure is known. The structure of tropine is represented by the following formula, which is that of a condensed pyridine and pyrrol nucleus. Tropic acid is condensed with the hydroxyl group of the base in the form of the ester.

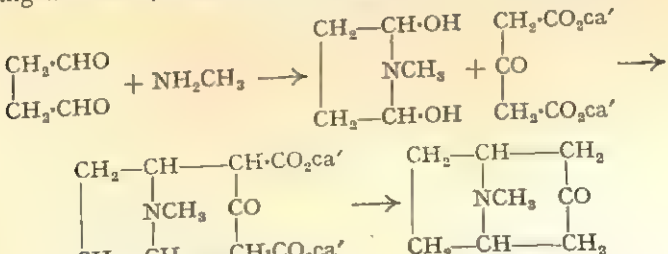


Tropine.



Tropic acid.

Tropine, which has a secondary alcohol group, yields *tropinone* on oxidation. The latter has been synthesised from succinic dialdehyde and methylamine mixed in aqueous solution with the calcium salt of acetone dicarboxylic acid. The product, on boiling with acid, loses CO_2 and gives tropinone (Robinson).

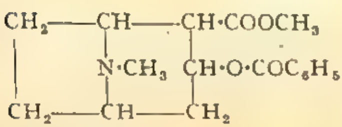


Calcium Tropinone dicarboxylate. Tropinone.

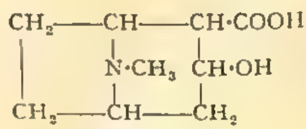
EXPT. 206. *Test for Atropine.*—Moisten a minute quantity of atropine with strong nitric acid, and evaporate it to dryness on the water-bath. Add to the yellow residue a few drops of alcoholic potash. A violet solution is obtained.

Cocaïne, $C_{17}H_{21}NO_4$.—The alkaloid is obtained from the leaves of *Erythroxylon coca,* in which several closely related alkaloids occur. The leaves are extracted with water, lead acetate is added to precipitate tannin and other substances; the filtered solution is then freed from lead by means of hydrogen sulphide; the filtered liquid is made alkaline, and the cocaïne extracted with ether. Cocaïne is a crystalline substance, which melts at 98°. The hydrochloride, $C_{17}H_{21}NO_4{\cdot}HCl$, is soluble in water, and is used in medicine as a powerful local anæsthetic. Taken internally, it acts as a strong poison. Cocaïne breaks up on hydrolysis into a base, ecgonine, methyl alcohol, and benzoic acid—

$$\underset{\text{Cocaïne.}}{C_{17}H_{21}NO_4} + 2H_2O = \underset{\text{Ecgonine.}}{C_9H_{15}NO_3} + C_6H_5COOH + CH_3OH.$$

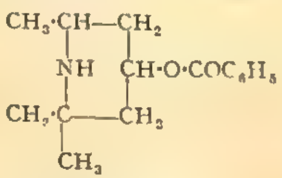


Cocaine.



Ecgonine.

As cocaine is very poisonous, it has been largely superseded by the synthetic alkaloids, β-eucaine, novocaine, and stovaine, which have the following structures—



β-Eucaine.

Novocaine, $(C_2H_5)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}OC{\cdot}C_6H_4NH_2$

Stovaine, $(CH_3)_2N{\cdot}CH_2{\cdot}C(CH_3)(C_2H_5)O{\cdot}OC{\cdot}C_6H_5$.

Quinoline Alkaloids

Cinchona Alkaloids.—The different varieties of cinchona bark which are grown in India, Ceylon, and South America are distinguished by the names of red, yellow, and pale bark, and contain a great number of alkaloids (amounting to 2 to 3 per cent. of the bark) united with quinic acid (p. 496) and a peculiar tannin, known as cinchotannic acid. The following are the most important members of the group—

$$\underset{\text{Quinine.}}{C_{20}H_{24}N_2O_2} \qquad \underset{\text{Cinchonine.}}{C_{19}H_{22}N_2O.}$$

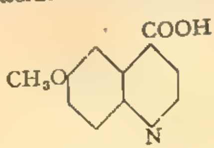
The well-ground bark is mixed with milk of lime and evaporated to dryness. The mass is extracted with chloroform or petroleum, and the extract shaken with dilute sulphuric acid, which dissolves out the alkaloids as sulphates. The acid solution is neutralised with ammonia and concentrated. Quinine sulphate first separates, whilst cinchonine sulphate remains in the mother-liquors.

Quinine, $C_{20}H_{24}N_2O_2$.—When the sulphate of quinine obtained as described above is dissolved in water and alkali added, the free alkaloid is precipitated, and may be purified by crystallisation from alcohol. It forms glistening white needles which, when anhydrous, melt at 177°. It has an alkaline reaction, a bitter taste, and is a feeble diacid base, forming a hydrochloride and sulphate of the following formulæ—

$$\underset{\text{Quinine sulphate.}}{C_{20}H_{24}N_2O_2{\cdot}H_2SO_4 + 8H_2O.} \qquad \underset{\text{Quinine hydrochloride.}}{C_{20}H_{24}N_2O_2{\cdot}2HCl + 2H_2O.}$$

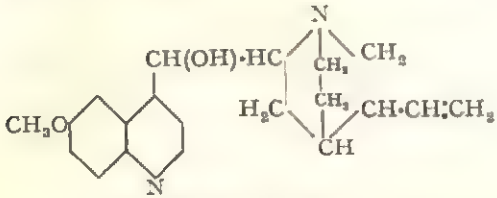
Quinine sulphate is the salt commonly used in medicine. It has the property of lowering the temperature, and is a valuable remedy in cases of malaria.

The structure of quinine is known. It is a tertiary diamine, for it combines with 2 molecules of methyl iodide. It yields quinoline when distilled with potash, and *quininic acid* when oxidised with chromic acid. The structure of quininic acid has the formula—



Quininic acid.

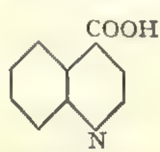
The whole structure is represented by the formula—



Formula of Quinine.

Expt. 207. *Tests for Quinine.*—Quinine is detected by the following tests. Use a solution of the hydrochloride prepared by adding a few drops of hydrochloric acid to the sulphate mixed with water. 1. Add to a little of the solution a few drops of iodine solution; a brown, amorphous precipitate is formed. This reaction is also given by other alkaloids (p. 579). 2. Add chlorine water and then ammonia in excess. An emerald-green colour is produced. 3. Add sodium carbonate solution and then a little ether. The free base is first precipitated, and then dissolves in the ether. Decant the ether on to a watch-glass and let it evaporate. Crystals of the base remain. 4. Dissolve a little quinine sulphate in a large volume of water, or add a few drops of glacial acetic acid and then a large volume of water. A blue, fluorescent liquid is obtained.

Cinchonine, $C_{19}H_{22}N_2O$, accompanies quinine in cinchona bark, and is especially abundant in the bark of *Cinchona huanoco,* which contains 2·5 per cent. It crystallises from alcohol in colourless prisms, and sublimes in a current of hydrogen in needles which melt at 250°. Its physiological action is similar to that of quinine, but less potent. On oxidation, cinchonine gives cinchoninic acid, or γ-quinoline-carboxylic acid—



Cinchoninic acid.

The other part of the molecule appears to be identical with that of quinine.

Cinchonine affords few distinctive tests. It may be distinguished from quinine by the absence of any colour reaction with chlorine and ammonia and the non-fluorescent character of its solutions.

Strychnos Alkaloids.—The seeds of nux vomica (*Strychnos nux-vomica*) and St. Ignatius' beans (*Strychnos Ignatii*) contain the three alkaloids strychnine, brucine, and curarine, which are remarkable for their excessively poisonous character. Their structure has not yet been fully explained. On distillation with potash they yield quinoline.

To obtain the alkaloids from nux vomica, the seeds are powdered and extracted with alcohol. The extract is concentrated, and lead acetate added to precipitate tannin. The excess of lead is removed from the filtrate with hydrogen sulphide, and the alkaloids are then thrown down from the filtrate with ammonia. Brucine is separated from strychnine by its greater solubility in alcohol.

Strychnine, $C_{21}H_{22}N_2O_2$, crystallises in colourless prisms, which melt at 284°. It is nearly insoluble in water, but dissolves readily in acids. The hydrochloride has the formula $C_{21}H_{22}N_2O_2 \cdot HCl$, and the alkaloid is therefore a monacid base.

EXPT. 208. *Test for Strychnine.*—A characteristic test for strychnine is the following:—Dissolve a crystal of strychnine in strong sulphuric acid, and add a little solid potassium dichromate, lead peroxide, or manganese dioxide. A violet colour is produced, which soon fades.

Brucine, $C_{22}H_{26}N_2O_4 + 4H_2O$, crystallises in colourless needles, which in the anhydrous state melt at 178°. When fused with potash, tetrahydroquinoline together with lutidine and collidine distil. It is a monacid base like strychnine, but is less poisonous.

EXPT. 209. *Test for Brucine.*—Brucine is detected as follows:—Dissolve a little brucine in strong sulphuric acid, and add a crystal of potassium nitrate or a drop of nitric acid. A deep orange colour is developed, which changes to violet on the addition of a solution of stannous chloride. The presence of nitric acid is easily detected by this reaction.

MORE COMPLEX ALKALOIDS.

Opium Alkaloids.—The milky juice of the poppy capsule (*Papaver somniferum*), when dried, constitutes *opium*, and is a complex mixture of a very large number of alkaloids, resins, proteins, mineral salts, and organic acids. The alcoholic solution of opium is known as *laudanum*.

The following is an average analysis of opium, only the more important alkaloids being given :—

	Per cent.		Per cent.
Morphine	10	Thebaïne	0·3
Narcotine	6	Narceïne	0·2
Papaverine	1	Meconic acid	4
Codeïne	0·5	Lactic acid	1·25

In order to separate the alkaloids, the opium is extracted with hot water and boiled with milk of lime, which dissolves the bases, but precipitates the meconic acid. The liquid is filtered from the insoluble calcium meconate, and the filtrate boiled with ammonium chloride until ammonia ceases to be evolved, whereby the lime is converted into calcium chloride and the morphine is precipitated together with other alkaloids.

Morphine, $C_{17}H_{19}NO_3+H_2O$, is a colourless, crystalline compound, which melts at 230° and decomposes at the same time. It is very slightly soluble in water, is without smell; it has a bitter taste, and is a strong narcotic. It has an alkaline reaction, and is a tertiary monacid base. The hydrochloride has the formula $C_{17}H_{19}NO_3 \cdot HCl + 3H_2O$. Morphine may be distinguished from many of the alkaloids by its solubility in caustic alkalis. There is little of a definite nature known about its structure. When distilled with zinc dust, it yields pyrrole, pyridine, quinoline, and phenanthrene.

Expt. 210. *Tests for Morphine.*—1. Add a few drops of ferric chloride to a solution of morphine chloride. A violet-blue colour is developed. 2. Add a little starch solution to a solution of morphine hydrochloride, and then a few crystals of iodic acid. Iodine is liberated by the morphine, and the starch turns blue. 3. Heat a little morphine with a few drops of strong sulphuric acid on the water-bath for half-an-hour. Cool the liquid, and add a drop of nitric acid. A violet colour is produced.

Questions on Chapter XL

1. Name some of the characteristic features of the alkaloids. What is the origin of the name?

2. How would you show the relation of certain of the alkaloids to pyridine and quinoline? Give examples.

3. Give either a general scheme or some special method for extracting the alkaloids from plants, and explain the object of the different steps.

4. What is piperine? What products does it yield on hydrolysis? Give a method for preparing pyridine from piperine.

5. Describe the synthesis of conine from pyridine.

6. How is nicotine prepared from tobacco? Name some of its properties. How would you show its relationship to pyridine?

7. What is tropine? How is it related to atropine? Name the plants in which atropine is found.

8. Describe a method for separating the cinchona alkaloids from bark. Compare the structure and reactions of quinine and cinchonine.

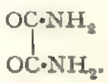
9. Name some of the constituents of opium. How are the alkaloids separated? What are the distinctive reactions for morphine?

10. How would you distinguish strychnine from brucine?

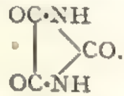
CHAPTER XLI

THE UREIDES

THE ureides are compounds derived from urea and belong to the class of amides. The ureide of oxalic acid or oxalyl urea may be compared with oxamide—

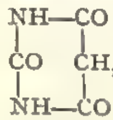


Amide of Oxalic acid, or Oxamide.

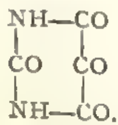


Ureide of Oxalic acid, Oxalyl urea, or Parabanic acid.

A large number of ureides of the dibasic acids are known, of which the following are examples—



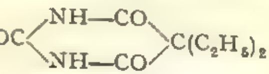
Malonyl urea, or Barbituric acid.



Mesoxalyl urea, or Alloxan.

Certain derivatives of malonyl urea have received important applications in medicine.

Veronal, the diethyl derivative, is an important hypnotic—



Veronal.

The dipropyl derivative, *propional*, and the diallyl derivative, *dial*, are used for the same purpose. Mesoxalic acid $CO(COOH)_2{\cdot}H_2O$ is obtained as a crystalline compound from the hydrolysis of dibrommalonic acid. The ureides of malonic acid and of mesoxalic acid can be used for the synthesis of **uric acid.**

Uric Acid, $C_5H_4N_4O_3$.—The composition of chalk stones and urinary calculi attracted the attention of physicians and alchemists at a very early period, and they speculated freely on their origin, submitting them to the usual process of dry distillation without eliciting much information. It is interesting to learn that Paracelsus looked upon them as deposits originating in the same manner as the lees, or tartar of wine. The discovery of uric acid, or, as it was then termed, *lithic acid*, in urinary concretions is due to Scheele, who in 1776 isolated the acid and observed the red colour which

it produces with nitric acid on evaporation. Prout subsequently noticed the change to violet which ammonia produces, now known as the *murexide* test. It is the principal test for uric acid.

EXPT. 211.—Evaporate a minute quantity of uric acid with a few drops of dilute nitric acid to dryness on the water-bath, then add to the red residue, when cold, a few drops of ammonia. A deep reddish-violet coloration is produced.

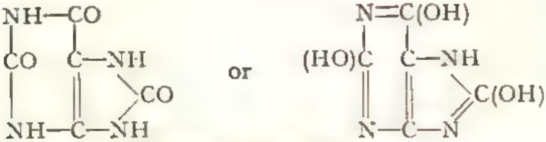
Uric acid is the chief constituent of the excreta of birds and reptiles. The excrement of snakes is nearly pure ammonium urate, $C_5H_3N_4O_3(NH_4)$. Guano contains a considerable quantity of uric acid together with guanine, which will be described later. The amount excreted by mammals is very small, not more than 0·2–1 gram being found in human urine in 24 hours. It is usually present in the urine as the acid ammonium salt; in the blood and calculi of gouty patients as the acid sodium salt, $C_5H_3N_4O_3Na$. It is precipitated from urine by adding 2 to 3 per cent. of strong hydrochloric acid and allowing the liquid to stand for a few days. Uric acid is usually obtained from snakes' or fowls' excrement or from guano. The material is boiled with caustic soda or potash until ammonia ceases to be evolved. The uric acid dissolves as the sodium salt, and the liquid is then filtered and the uric acid precipitated by the addition of a mineral acid.

Uric acid and the urates have a characteristic crystalline appearance, which is readily recognised under the microscope. Uric acid is very slightly soluble in water, but dissolves in caustic alkalis and in strong sulphuric acid without decomposition. It decomposes on dry distillation without fusion into ammonia, cyanuric acid, and urea.

Constitution of Uric Acid.—On oxidation with nitric acid, uric acid decomposes into alloxan and urea—

$$\underset{\text{Uric acid.}}{C_5H_4N_4O_3} + H_2O + O = \underset{\text{Alloxan.}}{C_4H_2N_2O_4} + \underset{\text{Urea.}}{CON_2H_4}.$$

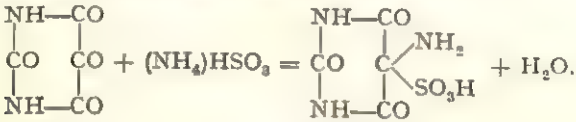
Now the structure of both alloxan and urea is known, and therefore uric acid must be represented by linking these two molecules together with the removal of two atoms of oxygen and hydrogen. This can be effected in several ways, but the following structural formula has, for various reasons, been adopted—



Tautomeric formulæ for Uric acid.

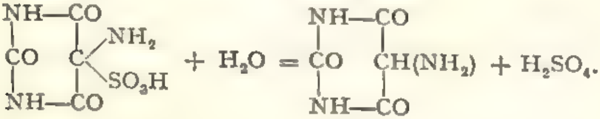
It explains the existence of four different monomethyl uric acids, of di- and tri-methyl uric acids and of one tetramethyl uric acid. From the latter, all the nitrogen is liberated as methylamine by heating with strong hydrochloric acid, and it follows that the 4 hydrogen atoms in uric acid are probably attached to nitrogen. This view of the structure of uric acid is supported by various syntheses, especially by that of E. Fischer. The steps in the synthesis are briefly the following. Alloxan and ammonium hydrogen sulphite form thionuric acid, which is decomposed by hydrochloric, or sulphuric acid, into uramil—

1.



Alloxan. Thionuric acid.

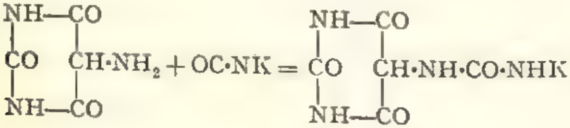
2.



Uramil.

Uramil and potassium cyanate unite to form potassium pseudo-urate—

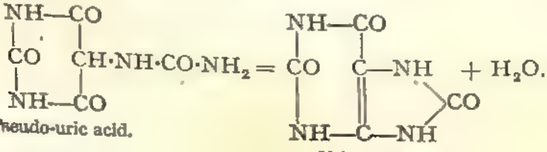
3.



Potassium pseudo-urate.

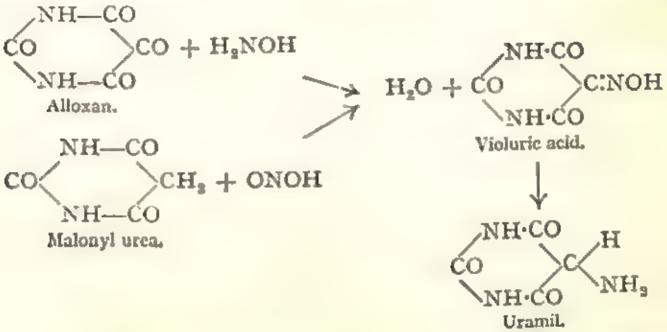
When the pseudo-uric acid is heated with 20 per cent. hydrochloric acid, it yields uric acid—

4.



Pseudo-uric acid.

The compound *uramil* can also be obtained from alloxan and hydroxylamine or from malonyl-urea and nitrous acid. The product in both cases is the oxime, *violuric acid*, which on reduction gives uramil—



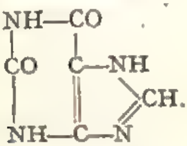
The question naturally arises: Why is uric acid an acid, seeing that it contains no carboxyl groups? Examples have already been given of organic substances, like acetoacetic ester and malonic ester, which contain hydrogen not forming part of a carboxyl group, being replaceable by metals. The present case resembles that of succinimide (p. 351). The hydrogen of the NH groups, probably from their proximity to carbonyl groups, become acidic and replaceable by metals. By the action of methyl iodide on these metallic compounds, the various methyl uric acids have been prepared.

Hypoxanthine, or *sarkine*, $C_5H_4ON_4$, is found in the blood and animal cells. It can be obtained from adenine (p. 594) by the action of nitrous acid.

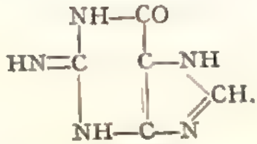
Xanthine, $C_5H_4N_4O_2$, is common to the vegetable and animal kingdom. It is present in extract of meat, in lupine seedlings, in malt, and in tea. It is closely related to uric acid; for though it contains one atom of oxygen less than uric acid, it yields the same products on oxidation, viz. alloxan and urea.

Guanine, $C_5H_5N_5O$, is obtained from guano by first extracting with boiling milk of lime. The residue is then heated with sodium carbonate, which dissolves the guanine. After precipitation with acetic acid, the guanine is purified by crystallising the hydrochloride from hot dilute hydrochloric acid. On oxidation it yields guanidine

(p. 341) and parabanic acid (p. 590). With nitrous acid it is converted into xanthine.

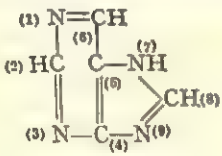


Xanthine.

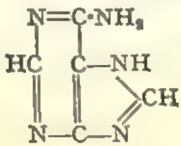


Guanine.

Adenine is related to guanine, and like guanine forms a constituent of animal and plant cells (p. 599). All these compounds and those that follow may be regarded as derived from the parent compound *purine*, which was synthesised by E. Fischer and shown by him to have the structure shown below. By reference to the small numerals in brackets, the positions of substituting groups are indicated; thus uric acid is 2·6·8-trioxypurine, guanine is 2-amino-6-oxypurine, and xanthine is 2·6 dioxypurine, etc.



Purine.



Adenine.

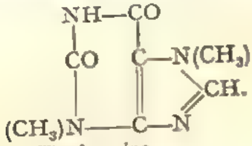
Adenine is 6-amino-purine.

Theobromine, 3·7-*Dimethylxanthine*, $C_7H_8N_4O_2$, is present in cocoa beans (*Theobroma cacao*) to the extent of 1–2 per cent. It has been synthesised from xanthine by acting with methyl iodide on the silver compound of xanthine.

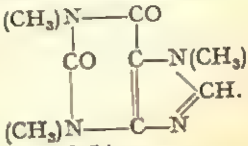
Theophylline, 1·3-*Dimethylxanthine*, $C_7H_8N_4O_2$, an isomer of theobromine, occurs in tea and is a strong diuretic. It has been synthesised from dimethyl urea, $CH_3NH{\cdot}CO{\cdot}NHCH_3$.

Caffeine, Theine, 1·3·7-*Trimethylxanthine*, $C_8H_{10}N_4O_2$, is present in coffee and tea. Coffee beans contain about 1 per cent., tea leaves from 1·5 to 2·5, or sometimes 3 per cent. of caffeine. It is readily prepared from tea as follows :—The tea is extracted with hot water, the albuminoid substances and tannin are precipitated with basic acetate of lead and removed by filtration. The excess of lead is then precipitated in the filtrate with sulphuric acid, and the caffeine extracted with chloroform. On evaporating the chloroform, the caffeine remains in the form of long silky needles. Caffeine has

been synthesised from theobromine and methyl iodide. In this way a third methyl group is introduced into xanthine. The following are the structural formulæ of theobromine and caffeine—

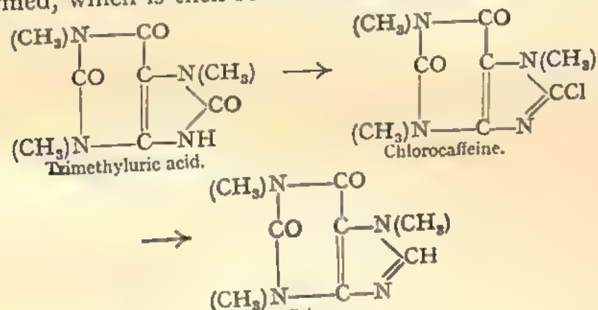


Theobromine.
(Dimethyl xanthine.)



Caffeine.
(Trimethyl xanthine.)

Both theobromine and caffeine have been prepared from uric acid by reducing the corresponding di- and tri-methyl uric acids. In the case of caffeine the process is as follows : Trimethyl uric acid, obtained by methylating uric acid, is acted upon with a mixture of phosphorus pentachloride and oxychloride. Chlorocaffeine is thus formed, which is then reduced with hydriodic acid—



Trimethyluric acid. Chlorocaffeine. Caffeine.

Questions on Chapter XLI

1. How do you obtain pure uric acid? What is the action of nitric acid upon uric acid?

2. Give the structural formula for uric acid, and show how, by oxidation with nitric acid, it yields alloxan and urea.

3. What is the nature of the bodies included in the uric acid group? Give a short sketch of the more important of these.

4. How is caffeine usually obtained? Describe its synthesis from uric acid.

5. Discuss the constitution of uric acid, including its synthesis. How do you account for its acid properties?

6. Explain the relations of xanthine, theobromine, and caffeine.

CHAPTER XLII

COMPOUNDS OF BIOLOGICAL IMPORTANCE

1. Proteins

Much attention is being paid to the study of compounds which enter into the life-process. Although the problems are extraordinarily difficult, much progress has been made, and terms like proteins and vitamins have long been household words. In this chapter a brief introduction to the subject is all that can be attempted.

Proteins.—The term protein (πρωτεῖον, first place) is used to denote many substances which make up the most important constituents of animal tissues and plant cells. They are highly complex compounds or mixtures of compounds, which are identified by chemical reactions, although it should be borne in mind that such reactions are characteristic of groups rather than of molecules. Proteins are colloidal substances of high molecular weight, and on hydrolysis the ultimate products are amino-acids. The percentage composition of the proteins varies somewhat as shown in the following table :—

C . .	50 to 55 per cent.	O . .	19 to 24 per cent.
H . .	6·9 to 7·3 ,,	S . .	0·3 to 2·4 ,,
N . .	15 to 19 ,,		

Phosphorus is also present in the so-called phospho-proteins. When burned, a small amount of mineral ash remains, but this is probably derived from adsorbed salts. Some of the simpler proteins—*e.g.*, egg albumin—dissolve in water and can be crystallised ; others, like globulin, though insoluble in water, dissolve in weak saline solutions. Phospho-proteins are acidic and dissolve in alkalis, but not in water.

The determination of molecular weights is rendered difficult

by the colloidal character and low solubility of the proteins. The most promising results have been obtained by means of a sedimentation process with the ultra-centrifuge. By this method it has been ascertained that the molecular weight of most of the proteins is either 17,600 or some simple multiple thereof. Proteins can be precipitated from solution by the process of "salting out" with ammonium sulphate, and since a definite concentration of this salt is needed for the precipitation of each protein, mixtures can be separated by fractional salting out. The protein suffers no permanent change in this process, and can be recovered unchanged on removal of the salt. Precipitation is most easily effected at what is called the *iso-electric point*. Proteins and amines, like many inorganic hydroxides, are amphoteric—that is, both basic and acidic—but an unusual feature of amino-acids and proteins is the production of bi-polar ions. Thus glycine gives the ion $H_3\overset{+}{N}{\cdot}CH_2C{\cdot}\bar{O}O$, which can absorb hydrogen ions in acid solution to form the cation $H_3\overset{+}{N}{\cdot}CH_2{\cdot}COOH$, or lose them in presence of alkali to form the anion $H_2N{\cdot}CH_2{\cdot}CO\bar{O}$. The iso-electric point is the point at which the two polarities of the bi-polar ion are equal, and is generally on the acid side.

Reactions of the Proteins.—Certain reactions are used to detect proteins, but as many of these are also given by simpler compounds, too much reliance should not be placed on any one reaction by itself.

1. A layer of concentrated nitric acid brought into contact with a protein will produce coagulation at the junction of the two liquids. Should the protein contain aromatic groups, a yellow colour will be formed on heating. On adding ammonia the colour becomes orange. This is the xanthoprotein reaction, and is given when nitric acid acts on the skin.

2. Proteins give precipitates with reagents which are also used to detect alkaloids (p. 579)—*e.g.*, phosphomolybdic and phosphotungstic acids, tannin, picric acid, and potassium mercuric iodide.

3. A solution of mercurous nitrate in excess of nitric acid (Millon's reagent) added to a solution of a protein containing a phenolic group gives a white precipitate, which turns red on heating.

4. A few drops of a solution of copper sulphate and an excess of caustic soda produce a violet colour, which becomes deeper in tint on

boiling. This is the *biuret* reaction (p. 339), and is given by many other compounds.

5. A violet colour is produced by adding a few drops of glyoxalic acid (p. 326) and concentrated sulphuric acid to proteins containing tryptophane groups (a derivative of indole). This is known as the Adamkiewicz–Hopkins reaction.

6. Coagulation of the soluble proteins is produced by the action of heat or on the addition of alcohol, acetone, or salts of alkaline earths or heavy metals. As precipitation is accompanied in this case by a rather obscure change known as denaturation, it is almost always irreversible. Coagulation takes place at a definite temperature which is characteristic of the protein and can be used for separation and even for quantitative determination. Denaturation of proteins is also caused by strong acids or alkalis. In this case the denatured products can be salted out, but are not coagulated by heat.

Classification of the Proteins.—It is found convenient to divide the proteins into groups, according to certain differences in their physical and chemical properties, but the line of demarcation is not sharp and different systems are in use. They may be classed in three main groups, viz.—(1) **simple proteins,** (2) **albuminoids,** (3) **conjugated proteins.**

Simple proteins are of many kinds. We can sub-divide them into (a) *albumins*, (b) *globulins*, (c) *plant proteins*, (d) *phospho-proteins*, and (e) *protamines.* Albumins such as egg albumin and serum albumin are soluble in water and are coagulated by heat. They are not precipitated from solution by the addition of sodium chloride or magnesium sulphate, but they can be precipitated by complete saturation with ammonium sulphate. Globulins, like *myosin* of muscle and *fibrinogen* of blood, are insoluble in water, but dissolve in weak saline solutions and also in dilute acids and alkalis. Globulins are completely salted out by magnesium sulphate, and they are also precipitated when their solutions are only half saturated with ammonium sulphate, by which means they can be freed from albumins. Plant proteins include *edestin* and the *gliadins*, which are richer in glutamic acid (p. 354) than other proteins. Phospho-proteins yield phosphoric acid when hydrolysed. They include *caseinogen*, the soluble calcium salt of which is present in milk, and *vitellin* of egg-yolk. Caseinogen and vitellin are insoluble in water, but dissolve in acids and alkalis. In the stomach caseinogen is converted by the ferment rennin to *casein.* Calcium

caseinate, unlike the caseinogenate, is insoluble in water and forms a curd. Protamines are products of hydrolysis of certain conjugated or nucleo-proteins present in the milt of fishes.

Albuminoids are the hard substances which make up the framework of animal bodies. Although closely allied to the simple proteins, they cannot be dissolved without decomposition, and they are usually resistant to the action of chemical reagents. They also differ more widely among themselves than the simple proteins. They are sometimes called *scleroproteins* (σκληρός, hard). Among them are *collagen*, the basis of cartilage and bone; *gelatine* or *glutin*, which is also present in bone; *keratin*, of which hair, nails, horns, etc., are composed; *elastin*, the substance of connective tissue; and *fibrosin* and *sericin*, the chief constituents of silk. Gelatine or glue is obtained from bones by dissolving out the inorganic matter (calcium phosphate) with dilute acid and heating the elastic mass, which retains the shape of the bone, with water under pressure. The substance dissolves, and on cooling sets to a jelly. Although gelatine does not give the ordinary reactions of proteins, it yields much the same products on hydrolysis with acids and alkalis or with enzymes. It forms an insoluble compound with tannin, a property used in the manufacture of leather (p. 495). When mixed with potassium dichromate and exposed to light, gelatine becomes insoluble in water. A number of photographic processes depend on this property. *Chitin*, the hard shell of the lobster, is sometimes classed with albuminoids, but it is known to be a carbohydrate derivative.

Conjugated Proteins.—The conjugated proteins are compounds of simple proteins with other complex compounds. Thus the nucleus of living cells contains compounds of proteins with nucleic acids, called *nucleo-proteins*. They are soluble in water and alkalis and in saline solutions, but they can be salted out. They are also denatured by heat. The nucleic acids have been resolved by hydrolysis with dilute mineral acids to phosphoric acid, a carbohydrate and purine bases, such as adenine (p. 594) and guanine (p. 373). **Chromo-proteins** are compounds of proteins with pigments containing iron. The best-known example is *hæmoglobin*, the red colouring matter of the blood, which combines with oxygen and carbon monoxide to give loose compounds, called *oxyhæmo-*

globin and *carboxyhæmoglobin*, respectively. The former plays an active part in respiration.

Constitution of the Proteins.—Although we are still unable to obtain a complete solution of the problem of the constitution of the proteins, much information has been collected by studying the products of hydrolysis and by the application of X-ray analysis. Hydrolysis breaks them down to give successively *albumoses*, *peptones*, *polypeptides*, and amino-acids. The latter all belong to a comparatively small group of α-amino-acids, of which the most important are glycine (p. 324), alanine and leucine (p. 326), aspartic and glutamic acids (p. 354), creatine (p. 326), and arginine, which is a derivative of α-amino-valeric acid and guanidine (p. 341) :—

$$HN{:}\overset{\overset{NH_2}{|}}{C}\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot \overset{\overset{NH_2}{|}}{C}H\cdot COOH.$$

Arginine.

Arginine is a decomposition product of the protamines (p. 598). The various amino-acids are most probably linked together by condensation of the carboxyl group of one molecule with the amino-group of another in the form of chains, which contain the grouping –CO–NH– several times repeated. Moreover, it is known that when two or more amino-groups are present in the amino-acid it is invariably the α-amino-group which is involved in the chain formation. These chain compounds are called *polypeptides*, the simplest of them, a dipeptide, being derived from two molecules of glycine, thus :—

$$H_2N\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot COOH.$$

Glycyl glycine.

As many as 18 molecules of amino-acids (15 of glycine and 3 of leucine) were artificially linked together by E. Fischer, to give an octadecapeptide, with a molecular weight of 1213. As the chains lengthen, the number of possible ways of linking them increases enormously, and as the molecular weight of Fischer's compound still falls far short of the value assigned to albumin, this method of approach to the problem is not very promising. Nevertheless it is known that polypeptides are found among the products of hydrolysis, and a polypeptide chain might reasonably be the struc-

ture of a fibre protein. The possibility of folding over of these chains is being investigated by X-ray analysis.

2. Vitamins

Vitamins.—It was discovered by Hopkins in 1906 that minute quantities of substances called vitamins are requisite accessories to the proteins, carbohydrates, fats, and salts that make up our foodstuffs, and which are not properly utilised in their absence. The vitamins are synthesised by plants, and in a few cases definite constitutions have been assigned to them, but they seldom occur singly, and their investigation is extremely difficult. Probably each individual vitamin has its own peculiar physiological action, just as each enzyme has to fulfil its own special chemical function. The different vitamins are distinguished by letters, the best known among them being vitamins A, B, C, and D; but these groups have had to be sub-divided. Vitamins A and D are soluble in fats, whilst B and C dissolve in water. *Vitamin A* is found in butter, yolk of egg, milk, and cod-liver oil, and is needed for the promotion of growth. It is a derivative of tetrahydrobenzene, with a long, unsaturated side-chain, containing one alcohol group. It is closely related to the polyene, carotene, $C_{40}H_{56}$ (p. 256), which occurs in carrots, and is probably formed from it by hydrolysis. Its empirical formula is $C_{20}H_{30}O$. *Vitamin B* is a complex mixture, and is present in all natural foodstuffs, but particularly in yeast. Certain processes used in the refining of food, such as the polishing of rice and the whitening of flour, result in the elimination of this important adjunct, which, like vitamin A, is essential to growth, and it is also disease resisting. *Vitamin C* has been identified by Haworth and Hirst as ascorbic acid—

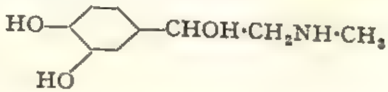
$$CH_2OH\cdot CHOH\cdot \overbrace{CH\cdot \underset{HO}{C}{:}\underset{OH}{C}\cdot CO}^{O}$$

It is anti-scorbutic, and is present in fresh fruits and some vegetables, but is easily destroyed by heat or by drying the fruit. *Vitamin D* is anti-rachitic, and is usually associated with vitamin A. It is formed from ergosterol (p. 602), a complex compound found in ergot and yeast, by irradiation with ultra-violet light.

3. Hormones

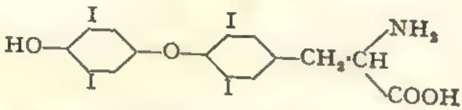
Hormones are substances secreted in the ductless glands of the body, and are transmitted directly into the blood.

Adrenaline, which occurs in the suprarenal gland, has been synthesised and has the constitution



The natural product is lævo-rotatory.

Thyroxine is an important secretion of the thyroid gland, and is rich in iodine. Harington and Barger have shown by synthesis that its constitution is



Insulin is a secretion of the pancreas, which regulates the concentration of sugar in the blood. Its molecular complexity is probably very great, and on hydrolysis it yields a number of amino-acids. It is often classed with the proteins.

4. Sterols and Bile Acids

Closely related to the vitamins are the sterols and the bile acids. Sterols are complex unsaturated alcohols, the most important of them being *cholesterol*, $C_{27}H_{45}OH$, *ergosterol*, $C_{28}H_{43}OH$, and *phytosterol*. Cholesterol was first discovered in gall-stones, but is present also in the brain, bile, yolk of egg and in lanoline, the fat of wool. Ergosterol is more unsaturated than cholesterol, and occurs in ergot and in yeast. Irradiation of ergosterol with ultra-violet light produces vitamin-D. The phytosterols occur in plants, and the bile acids are oxidation products of cholesterol.

5. Plant Pigments

Chlorophyll, the green colouring matter of plants, is now known to be a mixture of two pigments, of somewhat similar complex structure—viz., the blue-green chlorophyll-*a* and the yellow-green chlorophyll-*b*, each of which contains magnesium. The

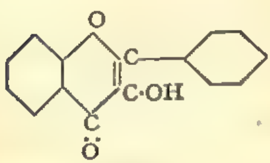
empirical formulæ are $C_{55}H_{72}O_5N_4Mg$, and $C_{55}H_{70}O_6N_4Mg$, respectively. These substances occur together with the orange-red carotene, $C_{40}H_{56}$ (p. 256) and a yellow crystalline compound *xanthophyll*, $C_{40}H_{56}O_2$. On hydrolysis, chlorophyll yields the unsaturated alcohol, *phytol*, $C_{20}H_{40}O$, and a complex heterocyclic compound derived from pyrrole (p. 565). It is known that chlorophyll plays an important part in the natural synthesis by plants of carbohydrates from carbon dioxide, formaldehyde being regarded as an intermediate product.

Carotene, $C_{40}H_{56}$ (p. 256), is an unsaturated hydrocarbon, and is closely related to vitamin A (p. 601).

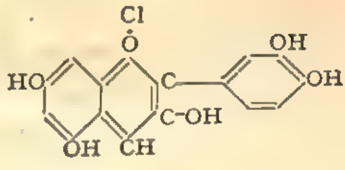
Xanthophyll, $C_{40}H_{56}O_2$, appears to be a hydroxy-carotene.

Anthocyanins are the colouring matter of flowers. On hydrolysis they yield glucose and anthocyanidins, some of which have been synthesised by Willstätter and by R. Robinson.

The anthocyanins may be regarded as hydroxy-derivatives of the same parent substance *flavonol*, combined with glucose. For example, the blue colour of the cornflower is due to the glucoside cyanin which on hydrolysis gives cyanidin or tetrahydroxy-flavonol, in which one atom of oxygen is replaced by hydrogen.



Flavonol.



Cyanidin chloride.

6. Enzymes

Enzymes.—The action of enzymes in fermentation has been described on p. 107. They are complex colloidal nitrogenous organic compounds, the nature of which is not yet fully known, since it is difficult to get them completely separated from other substances, chiefly carbohydrates, proteins, and salts with which they are associated. One property which distinguishes them from inorganic catalysts is their highly selective action. Thus α-methyl glucoside is hydrolysed by maltase, but not by emulsin, whereas

the β-glucoside is hydrolysed by emulsin, but not by maltase. E. Fischer explained this by suggesting that the structure of the enzyme must fit that of the compound attacked (now called the *substrate*) as exactly as a key must fit a lock. But the catalytic activity of a particular enzyme is not necessarily limited to one single reaction, for maltase reacts with other α-glucosides and emulsin with other β-glucosides. The activity of enzymes is greatly influenced by changes of temperature and of hydrogen-ion concentration. At low temperatures activity ceases, whilst at 100° C. the enzymes are destroyed. In most cases the optimum temperature lies between 25° and 38° C. Enzyme action is also reversible, and in some cases advantage has been taken of this fact to effect syntheses—*e.g.*, of cane-sugar. The number of known enzymes is very great. Their names are generally derived from those of the substrates by using the termination *-ase*, thus *urease* decomposes urea and *saccharase* hydrolyses saccharose. In a few cases, however, older, well-established names, such as *emulsin*, *ptyalin*, and *trypsin*, are still in use. The kinds of reaction which enzymes promote are numerous. Some induce hydrolysis; others (*oxidases* and *reductases*) promote oxidation or reduction; in some cases (e.g., *rennin*) coagulation results, and others again may bring about more complete degradation of the molecule than is involved in hydrolysis. Thus glucose may be split to give lactic acid, glycerol, acetaldehyde, or alcohol. The hydrolytic enzymes can be sub-divided into *proteolytic* enzymes such as pepsin and trypsin, which hydrolyse proteins; *lipolytic* (λίπος, fat) enzymes, like *lipase*, which act on fats; and those which hydrolyse carbohydrates, such as *amylase* or *diastase*, which resolves starch; and *saccharase* or *invertase*, which "inverts" cane-sugar.

Some of them have already been obtained in the crystalline condition—*e.g.*, urease, pepsin, and trypsin—but it is doubtful if any enzyme has yet been obtained quite pure, although it has been possible to increase their activity several hundred-fold by using physical methods to effect the removal of accessory compounds. E. Fischer supposed that enzymes were derived from proteins, but it has been found possible to purify them to such an extent that they cease to give any of the reactions characteristic of proteins, while fully retaining their enzymic character. The

most successful means of separating them from other colloids is by using either alumina or kaolin as adsorbents, according to whether the colloids carry electro-negative or electro-positive charges. Much further study of the enzymes will be needed before we can hope to understand the nature of the processes which occur in the living cells of plants and animals.

Questions on Chapter XLII

1. Give the reactions for the proteins. Describe some of their decomposition products.

2. Name some of the chief groups of proteins and their characteristic properties.

3. What is meant by the term *albuminoid substance?*

4. How is gelatine obtained? Name some of its properties. How could it be distinguished from egg-albumin?

5. What are the *polypeptides* and to what products do they give rise on hydrolysis?

6. Name some of the more familiar enzymes and indicate the nature of their chemical functions.

ANSWERS TO QUESTIONS

Chapter II

2. C, 42·13; H, 6·42; O, 51·45 per cent.
4. CO_2, 0·146; H_2O, 0·12; N, 74·66 c.c.
6. N, 45·92 per cent.
7. C, 39·78; H, 6·81 per cent.
10. N, 11·58 per cent.

Chapter III

1. $C_4H_8O_2$.
2. 120·05, M.W.
3. 192·7, M.W.
4. 91·45, M.W.
5. $C_3H_5ON_2ClS$.
6. CH_2O.
7. 177·3, M.W.
11. CH_2.
12. C_2H_6O.
13. C_6H_7N.

Chapter V

2. $n = 8$.
4. CH_4, 40; H, 55; N, 5 per cent.
17. CH_4, 42·25; H, 53·52; N, 4·23 per cent.
18. $C_{26}H_{54}$.

Chapter VI

1. 17·4; 7·9; 23·7; 14 grams.

Chapter XXII

4. 99 per cent.
12. $CH_3·CH(COOH)_2$, $CH_3·CH_2·COOH$.

Chapter XXXII

6. 20·32 per cent., or one *methoxyl* group.

INDEX

(Names of persons are printed in italics.)

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